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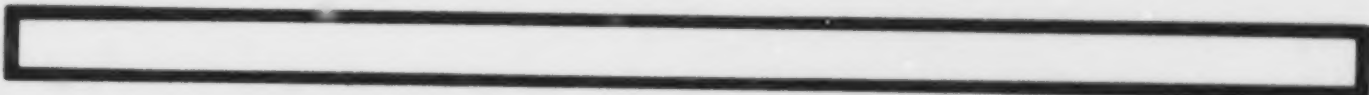
Stack Testing of the Mobile
Plasma Arc Unit

Alliance Technologies Corp., Bedford, MA

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STACK TESTING OF THE MOBILE PLASMA ARC UNIT

by

Mark Gollands, Edward Peduto, Joanna Hall, and Howard Schiff
Alliance Technologies Corporation
(Formerly GCA Technology Division, Inc.)
213 Burlington Road
Bedford, MA 01730

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EPA Project Officer
C. C. Lee

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HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
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16. ABSTRACT A trial burn program involving a plasma pyrolysis system was conducted at the Royal Military College, Kingston, Ontario. The plasma pyrolysis unit was developed by Pyrolysis Systems, Inc. under contract to the New York State Department of Environmental Conservation (NYSDEC). HWERL-Ci under a joint agreement funded the performance evaluation phase. Trial burns were conducted while firing carbon tetrachloride and polychlorinated biphenyls which are RCRA and TSCA regulated compounds respectively. Results from the trial burns indicate that the system is acceptable for treating these two compound classes in reference to the RCRA ($\geq 99.99\%$ DRE) and TSCA ($\geq 99.9999\%$ DRE) requirements.		
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NOTICE

This Final Report was furnished to the Environmental Protection Agency by the Alliance Technologies Corporation (formerly GCA Technology Division, Inc.), Bedford, Massachusetts 01730, in fulfillment of Contract No. 68-03-3243, Work Assignment No. 6. The opinions, findings, and conclusions expressed are those of the authors and not necessarily those of the Environmental Protection Agency or the cooperating agencies. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

FOREWORD

The Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of the environment and the interplay between its components require a concentrated and integrated attack on the problems.

Research and development is the first necessary step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Hazardous Waste Engineering Research Laboratory develops new and improved technology and systems to prevent, treat, and manage hazardous waste pollutant discharges. This publication is one of the products of that research.

This document presents information which can be used to assess the feasibility of destroying hazardous waste using a mobile plasma pyrolysis unit. Trial burns involving RCRA and TSCA regulated compounds were conducted during which time all environmental release points were sampled and actual release rates quantified.

Thomas R. Hauser, Director
Hazardous Waste Engineering
Regional Laboratory

ABSTRACT

The mobile plasma arc system developed by Pyrolysis Systems, Incorporated (PSI) underwent an extensive trial burn program in Kingston, Ontario, Canada. The objectives of this program were to evaluate the performance of the system and to establish its destruction and removal efficiency (DRE) capabilities while pyrolyzing both RCRA and TSCA regulated hazardous waste feeds. The emissions were sampled and analyzed for: carbon tetrachloride (CCl_4), hydrogen chloride (HCl), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), and particulate matter. Of notable concern were polynuclear aromatics (PNAs) contained in the scrubber water discharge. Samples of the scrubber water generated during the system operations were also analyzed for CCl_4 , HCl , PCBs, and PCDD/PCDF.

During the CCl_4 trial burns, the pyrolysis system met the established RCRA requirement with a DRE of CCl_4 of greater than 99.99 percent. The CCl_4 emissions averaged 24.98×10^{-6} kg/hr with an average input of 63.0 kg CCl_4 /hr. HCl emissions averaged 0.35 kg/hr. NO_x and CO emissions were 0.35 and 0.14 kg/hr, respectively. CCl_4 discharged through the scrubber water averaged only 6.21×10^{-6} kg/hr.

Results of the PCB trial burns indicate that the pyrolysis system destroyed the PCBs at a level of greater than or equal to 99.9999 percent DRE. PCB stack emissions during the three test runs ranged from Not Detected (ND) to 0.11×10^{-6} kg/hr with a system DRE of greater than 99.9999 percent. PCDD and PCDF emissions were in ranges of ND to 0.028×10^{-6} kg/hr (PCDD) and 0.082×10^{-6} to 0.304×10^{-6} kg/hr (PCDF). HCl and particulate matter emissions averaged 0.0039 and 0.028 kg/hr, respectively. NO_x and CO emissions averaged 0.476 and 0.053 kg/hr, respectively. PCDDs were not detected in the scrubber water discharge. PCDFs were detected in very small concentrations in only the first test run. PCBs discharged in the scrubber water ranged from ND to 93.1×10^{-6} kg/hr. PNA concentrations in the ppb range were detected in both the spent scrubber water and the stack gas.

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SECTION 1

INTRODUCTION

The U.S. Environmental Protection Agency's Hazardous Waste Engineering Research Laboratory (HWERL), Cincinnati, Ohio, and the New York State Department of Environmental Conservation (NYSDEC) established a Cooperative Agreement in 1982. The Cooperative Agreement called for the construction and testing of a mobile pilot-scale plasma arc system for the high efficiency destruction of hazardous waste. The capacity of the system is nominally designed to be four kilograms (8.8 pounds) per minute, and to fit, with ancillary equipment, in a 45 foot trailer. The concept of the plasma arc is that it uses very high intensity energy with temperatures approaching 10,000°C to break bonds of hazardous waste chemical molecules down to the atomic state. The recombination of these atoms results in molecules such as hydrogen, carbon monoxide, carbon dioxide and hydrochloric acid. The off-gases from the plasma system are subsequently scrubbed to remove hydrochloric acid and flared to remove combustibles.

In general, the approach taken for this EPA/NYSDEC Cooperative Agreement involves four phases of activity. Implementation of each phase was subject to the EPA/NYSDEC approval of the preceding phase results. The first two phases were performed in Canada with the cooperation of Canadian Federal, Provincial and local authorities; the third and fourth phases will be performed in the state of New York. The total Cooperative Program is configured as follows:

- Phase I: Construction and shakedown of the mobile plasma arc system by the vendor, Pyrolysis Systems, Inc. (PSI).
- Phase II: Performance testing of the plasma system at the Kingston, Ontario test site (GCA involvement).
- Phase III: Transportation, installation and verification of system performance at a site in New York State.
- Phase IV: Demonstration tests as designated by NYSDEC for permitting purposes at a New York State hazardous waste site.

The vendor, Pyrolysis Systems, Inc., completed the construction and shakedown phase (Phase I) at the Kingston, Ontario test site by December 1984. The unit was then suitable for the initiation of the Phase II performance tests.

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GCA's involvement began with the initiation of Phase II sampling activities in February 1985. Several postponements occurred prior to this time which further delayed preparatory activities and eventual mobilization of the test crew and equipment. Mobilization and the initiation of Phase II activities were finally accomplished in February 1985.

Phase II consisted of several stages of performance testing. Stage I included equipment operation and shakedown which was performed by PSI prior to GCA's arrival onsite. Stage II and Stage III were further broken down into several test series which were designed to assess system performance using different waste feeds. Stage II testing utilized carbon tetrachloride (CCl_4) as the waste feed component during three 60 minute test burns (Test Series 1). CCl_4 destruction and HCl removal were the primary goals during these performance tests. Stage II testing concluded in February 1985.

Stage III testing utilized an Askarel waste feed blend to prove the system's performance capabilities for PCB destruction. Testing under Stage III Test Series 2 was not conducted by GCA. The system was proven acceptable for further endurance testing during the three 60 minute tests conducted by IMET, a local test company, during the period December 1985 to February 1986. Stage III, Test Series 3 was initiated and completed during February 1986 by GCA. These three endurance tests were originally scheduled to be 6 hour test burns with the system's waste feed consisting of the Askarel blend. The first attempt ended prematurely due to a system shutdown. When the first endurance burn attempt ended after only 115 minutes, the target time for the remaining tests was shortened to 4 hours. Only two full term endurance tests were completed during this test series.

Measurement activities during Stages II and III were conducted in order to obtain information on the effectiveness of the plasma arc, scrubber, and flare systems in destroying or removing certain compounds of interest present in the waste feed. These activities also served to assess the reliability of system components and the stability of destruction performance.

SECTION 2

SUMMARY, DISCUSSION OF RESULTS, AND CONCLUSIONS

PROJECT SUMMARY

The measurement activities were conducted in accordance with the Quality Assurance Project Plan (QAPP, Reference 1) which was prepared and submitted under EPA Contract No. 68-02-3698, Task No. 011. Any deviations from this QAPP have been addressed in Section 7 of this report.

The primary purpose of Stage II was to demonstrate destruction capabilities of waste materials containing regulated chain chlorinated compounds. One test series was conducted and involved three 60 minute tests. The only waste feed component was CCl_4 contained in an MEK, methanol, and water blend. The primary purpose was to demonstrate proper HCl removal through the scrubber process and the destruction of one of the harder to destroy compounds (CCl_4).

The Stage II sampling and analytical parameters are shown in Table 2-1. The various samples were collected and analyzed onsite. Spent scrubber water was stored in one cubic meter tanks pending completion of the onsite analyses and a demonstration of compliance with the Ontario Ministry of the Environment (MOE) effluent guidelines.

The primary purpose of Stage III was to demonstrate the destruction capabilities of the system using a waste feed containing more complex chlorinated aromatic compounds, namely Askarel. The Askarel was comprised of a mixture of three Aroclors and trichlorobenzene with the balance of the waste feed being MEK and methanol.

Stage III Test Series 2 consisted of three 60 minute test burns which were monitored by IMET. Testing was initiated in December 1985 and was completed by February 1986. As GCA had no involvement in these 1 hour PCB burns, no data from these burns are presented in this report. GCA was mobilized and onsite again in February 1986 to begin Stage III Test Series 3 which consisted of three 6-hour endurance test burns. Due to the possibility of system malfunctions and lengthy delays, the sampling period was shortened to 4 hours. Testing commenced on February 12 and ended February 22, 1986. The first test lasted 115 minutes (1 hr 55 min) before shutting down due to a torch power malfunction. The second test on February 20 lasted for the full 4 hours, as did the third and final burn on February 22. The parameters measured during Stage III Test Series 3 are shown in Table 2-2.

TABLE 2-1. STAGE II, TEST SERIES 1 SAMPLING PARAMETERS

Sampling point	Measurement parameter
Postflare product gas	O ₂ , CO, CO ₂ , HCl, NO _x , CCl ₄ , flue gas velocity and temperature
Spent scrubber water	CCl ₄
Waste feed	Sample and archive
Reactor ash	Sample if available and archive

TABLE 2-2. STAGE III, TEST SERIES 3 SAMPLING PARAMETERS

Sampling point	Measurement parameters*
Postflare product gas	O ₂ , CO ₂ , CO, NO _x HCl, particulate matter semivolatiles, VOCs, PCDDs/PCDFs, PCBs, TCBS flue gas velocity, temperature, moisture
Spent scrubber water	semi-VOCs, VOCs, TCBS, PCBs, PCDDs/PCDFs
(Reactor ash)	if available
Waste feed	PCDDs/PCDFs, PCBs, TCBS

*VOCs = volatile organic compounds

PCDDs = polychlorinated dibenzo-p-dioxins

PCDFs = polychlorinated dibenzofurans

PCBs = polychlorinated biphenyls

TCBs = total chlorinated benzenes

The data are reported in essentially two parts. The first represents data obtained during Stage II, Test Series 1 during which time carbon tetrachloride was the selected principal organic hazardous constituent (POHC). These data include scrubber waste feed, water, and stack gas parameters obtained during the testing. The second data group represents information obtained under Stage III Test Series 3 during which an Askarel waste blend was the selected waste feed.

CARBON TETRACHLORIDE TRIAL BURN

Sampling for CCl_4 emissions was conducted during Stage II, Test Series 1 to determine the overall CCl_4 destruction and removal efficiency (DRE) of the system. CCl_4 was selected as the principal organic hazardous constituent (POHC) because its very low heat of combustion suggests it is a difficult material to be thermally destroyed, based on EPA's current ranking guidance (Reference 2); it is readily available, and it is relatively inexpensive. Consequently, trial burns are frequently conducted using CCl_4 as the POHC. Testing was initiated on February 16, 1985, after 4 days of plasma arc system preparation and test equipment set up. The test schedule was as shown in Table 2-3. The results from the three completed 60 minute test runs are shown in Tables 2-4 and 2-5.

During the three tests, waste feed rates of 2.82, 2.26 and 2.83 liters per minute, respectively, were introduced to the system. This corresponds to mass feed rates of 64.2, 60.6, and 64.2 kilograms CCl_4 per hour (kg/hr), respectively. Scrubber water flow rates during these tests were, respectively 33, 30, and 32 liters per minute (L/min). Stack gas flow rates during these tests were 38.13, 29.69, and 29.81 dry standard cubic meters per minute (m^3/min).

Waste Feed - CCl_4 /MEK/MEOH

The waste feed blend of CCl_4 and methyl ethyl ketone was introduced at rates averaging 2.82, 2.26, and 2.83 L/min. These correspond to CCl_4 mass feed rates of 64.2, 60.6, and 64.2 kg/hr. These figures were used in calculating the destruction and removal efficiency (DRE) of the system shown in Table 2-4.

Scrubber Water

Scrubber water samples were taken and analyzed for CCl_4 concentrations which were then combined with scrubber water flow rates to yield CCl_4 discharged to the sewer. The concentrations of CCl_4 found in the scrubber water were 1.27, 5.47, and 3.26 ppb ($\mu\text{g}/\text{L}$), respectively, for the three 1-hour tests. The mass discharge rates are presented in Table 2-4.

Postflare Stack Gas

During the CCl_4 waste feed burns, samples of the postflare stack gas were obtained and analyzed for HCl and CCl_4 . In addition to these parameters, the stack gas flow rate, temperature, and bulk gas constituents (O_2 , CO , CO_2 and NO_x) were monitored on a continuous basis.

TABLE 2-3. CCl₄ TEST BURN SCHEDULE

Date (1985)	Occurrence	Test Duration (min)	Comments
2/16	1st burn	15	System malfunction
2/18	2nd burn	60	1st complete test run
2/23	3rd burn	26	System malfunction
2/24	4th burn	38	System malfunction
2/26	5th burn	60	2nd complete test run
2/26	6th burn	60	3rd complete test run

TABLE 2-4. STAGE II CCl₄ AND HCl EMISSIONS

	Run 1	Run 2	Run 3	Average
Date, 1985	2/18	2/26	2/26	
Test duration, min.	60	60	60	60
<u>Waste Feed Parameters</u>				
Waste Feed Composition				
CCl ₄ , mass %	35	40	35	36
MEK/MeOH	65	60	65	64
Specific gravity				
kg/L	1.08	1.12	1.08	1.09
Waste Feed Flow Rate,				
L/min	2.82	2.26	2.83	2.64
kg/min	3.05	2.53	3.06	2.88
CCl ₄ Feed Rate, kg/min	1.07	1.01	1.07	1.05
kg/hr	64.2	60.6	64.2	63.0
<u>Scrubber Water Parameters</u>				
Discharge Flow Rate,				
L/min	33	30	32	32
CCl ₄ Concentration,				
ppb (ug/L)	1.27	5.47	3.26	3.33
CCl ₄ Discharge Rate,				
kg/hr	2.51x10 ⁻⁶	9.85x10 ⁻⁶	6.26x10 ⁻⁶	6.21x10 ⁻⁶
lb/hr	5.54x10 ⁻⁶	21.71x10 ⁻⁶	13.80x10 ⁻⁶	13.68x10 ⁻⁶
<u>Stack Gas Parameters</u>				
Average Flow Rate, m ³ /min ^a	38.13	29.69	29.81	32.54
ft ³ /min ^a	1,346.3	1,048.3	1,052.7	1,149.1
Average Temperature °C	908	821	692	807
°F	1,666	1,510	1,277	1,484
HCl Conc., mg/m ^{3a}	b	138	247	193
HCl Emissions, kg/hr	N/A	0.25	0.44	0.35
lb/hr	N/A	0.55	0.97	0.76
CCl ₄ Conc., ppb ^c	c	c	c	c
CCl ₄ Emissions, kg/hr	29.27x10 ⁻⁶	22.79x10 ⁻⁶	22.89x10 ⁻⁶	24.98x10 ⁻⁶
lb/hr	64.39x10 ⁻⁶	50.14x10 ⁻⁶	50.36x10 ⁻⁶	54.96x10 ⁻⁶
System CCl ₄ DRE, %	>99.99	>99.99	>99.99	>99.99

^aDry standard conditions as defined by 20°C and 760 mm Hg.

^bHCl sampling conducted at preflare location. Sampling suspended due to carbon plugging of train (not analyzed).

^cResults are based on estimated detection limit of 2 ppb. Actual detection limit was in the range of 2-15 ppb and was not quantified.

TABLE 2-5. COMBUSTION PARAMETERS - CCl₄ TRIAL BURNS

Test run	1	2	3	Average
Date, 1985	2/18	2/26	2/26	
Stack Gas m ³ /min ^a	38.13	29.69	29.81	32.54
Flowrate ft ³ /min ^a	1,346.3	1,048.2	1,052.7	1,149.1
Stack Gas Temperature, °C	908	821	692	807
°F	1,666	1,510	1,277	1,484
NO _x Concentration, ppm (v/v)	106	92	81	93
Emission Rate, kg/hr	0.46	0.31	0.28	0.35
lb/hr	1.02	0.69	0.62	0.78
CO Concentration, ppm (v/v)	48	57	81	62
Emission Rate, kg/hr	0.13	0.12	0.17	0.14
lb/hr	0.28	0.26	0.37	0.30
O ₂ , percent	12.7	14.4	15.1	14.1
CO ₂ , percent	6.0	5.7	4.9	5.5

^aDry standard conditions as defined by 20°C and 760 mm Hg.

HCl--

During Run 1, hydrogen chloride was sampled at the preflare location (see Figure 5-6) but was aborted after 20 minutes due to plugging of the sample line by the high carbon and moisture content of the gas stream. This sample was invalidated. No further testing was attempted at this location after several flarebacks occurred, causing safety concerns at this sampling location. The sample train utilized in obtaining the HCl samples is described in Section 4.0. The concentrations of HCl found in the stack gas were 137.7 and 247.2 mg/m³ for Runs 2 and 3, respectively. The results of the HCl testing are further summarized in Table 2-4.

Carbon Tetrachloride--

CCl₄ samples were obtained from the stack gas using an integrated bag sampling technique whereby a volume of stack gas was drawn into a Tedlar bag at a constant rate over a period of time. The gaseous samples were then subjected to onsite analyses by gas chromatography equipped with an electron capture detector (GC/ECD). The concentrations of CCl₄ present in the stack gas during Runs 1, 2 and 3 were all below the detection limit of the analytical instrument (less than 2 ppb). For the purposes of this report, and the establishment of a reportable DRE for the system while fired with a CCl₄-containing waste feed, CCl₄ emission rates of 29.27×10^{-6} , 22.79×10^{-6} , and 24.98×10^{-6} kg/hr were used in the calculations. The DRE is calculated using only the stack gas emission rate and does not include CCl₄ discharged in the scrubber water. Therefore, the established DRE's for Runs 1, 2, and 3 are all greater than 99.99 percent. Table 2-4 contains a summary of the stack gas data including the system's DRE.

O₂, CO₂, CO and NO_x--

In addition to HCl and CCl₄ sampling and analysis, combustion parameters were measured in the postflare stack gas via GCA's continuous emission monitor system (CEMS). Samples were extracted on a continuous basis by means of an in-stack probe, filter, and heated sample line and passed through a gas conditioning system and valving system to the calibrated analyzers. The gas streams were analyzed for O₂, CO₂, CO, and NO_x concentrations. Resultant data (millivolt output) were input directly to the Fluke Data Acquisition System and strip chart recorder. The Fluke output was formatted into test report form and yielded results in ppm, percent, and pounds per hour, as necessary. In addition, stack gas velocity was recorded continuously via a pitot tube/pressure transducer hookup to the Fluke computer system. Temperature was monitored similarly using a thermocouple/Fluke hookup. All test combustion data are summarized in Table 2-5.

As is the case with most combustion sources, NO_x and CO are good indicators of combustion temperatures and efficiency. During startup and shutdown operations, the flare is quite unstable due to the nonsteady reactor product gas supply. This is due largely to the fact that, during startup, the reactor requires a minimum time period to reach equilibrium temperature. Because of the instability upon startup, the system was brought up to operating temperatures on a waste feed containing nonchlorinated compounds, such as methyl ethyl ketone (MEK). Once online and up to temperature, the chlorinated waste was then introduced. There was usually a slight instability

in the system as the new waste entered the plasma as may be evidenced by changes in the postflare stack gas temperatures and concentrations of O₂, CO₂, and NO_x. Generally, once system temperatures stabilized, CO concentrations were relatively constant at levels of less than 0.17 kg/hr. Different types of waste, and even the same waste with slightly varying compositions, seemed to affect varying system responses. As such, although the system could be controlled to operate within a certain range, the repeatability of tests using different waste feeds remains a question. This is due, in part, to the chlorine composition, density, and solids content found in different types of liquid waste feeds.

PCB TRIAL BURN

GCA's involvement during Stage III began with Test Series 3 wherein sampling took place during the conduct of three endurance PCB trial burns. The waste feed during these burns was comprised of a blend of three Aroclors, trichlorobenzene, methyl ethyl ketone, and methanol. Askarel (Aroclor/trichlorobenzene blend) comprised approximately 25 percent of the waste feed by weight. Test Series 3 was included in the program to test the plasma pyrolysis system over a period of 4 hours while a waste of this type was introduced. Originally, three 6-hour runs were slated for this test series. However, the target run times were reduced to four hours in a joint decision by PSI and NYSDEC personnel in an effort to conserve waste feed and to complete the sample runs in a timely manner. This shortened run time was also deemed sufficient for allowing adequate detection limits for the required analytical parameters.

During the first trial burn (GCA Run 3-1, February 12, 1986), sampling ended after 115 minutes (1 hr 55 min.) due to torch power problems within the pyrolysis system. The second and third burns (GCA Runs 3-2 and 3-3, February 20 and 22, 1986, respectively) were each completed after 240 minutes (4 hours) of sample time. During Run 3-2, sampling was interrupted for approximately 30 minutes due to an offsite power grid loss causing a system upset. The system was brought back on line with the MEK/MEOH waste feed and sampling was resumed 10 minutes after the switch back to the PCB waste feed blend was made. During all operation of the pyrolysis system, no PCB containing waste was introduced prior to the system first being stabilized on the MEK/MEOH feed. Additionally, no sampling was conducted while the system was solely on the MEK/MEOH feed, in transition to the PCB waste feed, nor during a system upset period. The test schedule for Stage III Test Series 3 was as shown in Table 2-6. The resultant data from these test runs are presented in this section.

During the three test runs, the PCB waste blend was introduced to the system at rates of 2.10, 2.33, and 2.20 kilograms per minute (kg/min), respectively. The average PCB content of this feed (total, mono through decachlorinated biphenyls) was 12.6 percent by weight. The total mass PCB input was 0.26, 0.29, and 0.28 kg/min., respectively, for the three runs. Scrubber water flow rates averaged 36.5, 33.0, and 32.5 liters per minute (L/min). Stack gas flow rates were 45.43, 36.41, and 35.81 dry standard cubic meters per minute (m³/min), for Runs 3-1, 3-2, and 3-3, respectively.

TABLE 2-6. PCB TEST BURN SCHEDULE

Date	Occurrence	Test duration (min)	Comments
2/12/86	1st burn	115	Run 3-1 abbreviated due to system malfunction.
2/20/86	2nd burn	240	Run 3-2 interrupted for about 1/2 hr-completed
2/22/86	3rd burn	240	Run 3-3, slight fan problems during port change but no interruption-completed.

Waste Feed - Askarel/MEK/MEOH

The PCB waste feed blend was introduced at an average rate of 2.21 kg/min with a PCB mass input of 0.28 kg/min or 16.7 kg/hr. This mass input includes mono through decachlorinated biphenyls. Integrated samples were obtained during each test run from the valving assembly just prior to the feed ring of the reactor vessel. At this point, the waste feed blend was well mixed and representative of that fed into the plasma reactor. The samples were analyzed for total PCBs, chlorobenzenes, polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). Data on waste feed composition and feed rate are presented in Table 2-7.

Scrubber Water

Scrubber water samples were collected during each test run and analyzed for volatile and semivolatile compounds including PCBs and PCDDs/PCDFs. During Runs 3-1, 3-2, and 3-3, scrubber water flow rate was 36.5, 33.0, and 32.5 L/min, respectively. The scrubber water samples were analyzed by GCA's laboratory and the resultant data are summarized in the following paragraphs.

Volatiles--

The volatile compounds found in the scrubber water were principally benzene, toluene, chlorobenzene, and styrene. Their mass emission rates, based on their aqueous concentrations ($\mu\text{g/L}$) and the scrubber discharge rate are shown in Table 2-8. In addition to those compounds listed above, two others were detected albeit at concentrations beneath the detection limit of the instrument. These were trans 1,2-dichloroethene in Run 3-2 and chloroform in Run 3-3. Chloroethane and 2-butanone were also found in Run 3-3 in measurable quantities. The scrubber water sample from Run 3-1 was lost due to freezing and breakage of the VOA vials.

Semivolatiles--

Semivolatile components of the scrubber water discharge were sampled by means of compositing samples in a large container during the course of each test run. Samples were split in order that a large aliquot could be sent to Zenon Environmental, Inc. to conduct the PCB, chlorobenzene, and PCDD/PCDF analyses. These data are presented and discussed separately. The remaining aliquots were transported to GCA's laboratory to conduct further semivolatile analyses. Generally, the compounds detected and quantified are sister compounds to naphthalene and pyrene. They are presented in Table 2-9 with their associated concentrations and mass discharge rates. The concentrations presented in this table are combined aqueous and carbon analyzed matrices, as the samples were two-phased. Generally, the carbon layer had higher concentrations of semivolatile compounds than the aqueous phase. In most cases, the carbon separated from the aqueous solution, forming a top layer with a light, meringue-type consistency. In other samples, the carbon remained in suspension or gradually settled out over a period of time. This inconsistency in carbon layer formation may be due to varying consistency of the scrubber water in which the density of the carbon is greater than that of the aqueous solution phase. Additional analytical data are presented in subsequent sections.

TABLE 2-7. WASTE FEED COMPOSITION AND FEED RATE

Date	Run No.	PCB content ^a percent	Waste feed flow rate (kg/min)	PCB mass input (kg/min)
2/12/86	3-1	14.3 ^b	2.10	0.30
2/20/86	3-2	12.5 ^b	2.33	0.29
2/22/86	3-3	12.8 ^b	2.20	0.28

^aTotal PCBs (mono-decachlorinated biphenyls).

^bFrom Zenon's analyses.

TABLE 2-8. SCRUBBER WATER - VOLATILE MASS EMISSION RATES

Date	Run #	Compound	Concen- tration ($\mu\text{g/L}$)	Scrubber water flow rate (L/min)	Compound mass emission rate (10^{-6} kg/hr)
2/20/86	3-2	1,2-dichloroethene	2 ^a	33.0	4
		Benzene	840		1,663
		Toluene	41		81
		Chlorobenzene	83		164
		Styrene	86		170
2/22/86	3-3	Chloroethane	23	32.5	45
		Chloroform	3 ^a		6
		Benzene	770		1,502
		Toluene	29		57
		Chlorobenzene	50		98
		2-butanone	12		23
		Styrene	68		133

^aComponent present beneath detection limits. Results should be considered semiquantitative.

TABLE 2-9. SCRUBBER WATER - SEMIVOLATILE MASS EMISSION RATES

Date	Run #	Compound	Concentration ($\mu\text{g/L}$)	Scrubber water flow rate (L/min) ^a	Compound mass emission rate (10^{-6} kg/hr)
2/12/86	3-1	Napthalene	21,000	36.5	45,990
		Acenaphthalene	72,000		157,680
		Acenaphthene	240		526
		Fluorene	1,500		3,285
		Phenanthrene	35,000		76,650
		Anthracene	160		350
		Fluoranthene	21,000		45,990
		Pyrene	21,000		45,990
		Benzo (A) Anthracene	1,200		2,628
		Chrysene	1,900		4,161
		Benzo (B) Fluoranthene	1,800		3,942
		Benzo (K) Fluoranthene	1,000		2,190
		Benzo (A) Pyrene	3,200		7,008
		Indeno(123-CD) Pyrene	3,600		7,884
		Benzo(GHI) Perylene	7,700		16,863
		2-Methylnapthalene	40		88
2/22/86	3-2	Napthalene	11,000	33.0	21,780
		Acenaphthalene	54,000		106,920
		Acenaphthene	340		673
		Fluorene	1,400		2,772
		Phenanthrene	28,000		55,440
		Anthracene	1,300		2,574
		Fluoranthene	20,000		39,600
		Pyrene	16,000		31,680
		Benzo (A) Anthracene	1,000		1,980
		Chrysene	1,600		3,168
		Benzo (B) Fluoranthene	1,300		2,574
		Benzo (K) Fluoranthene	860		1,703
		Benzo (A) Pyrene	2,700		5,346
		Indeno (123-CD) Pyrene	2,600		5,148
		Benzo (GHI) Perylene	5,100		10,098
		2-Methylnapthalene	300		594

(continued)

TABLE 2-9 (continued)

Date	Run #	Compound	Concentration ($\mu\text{g/L}$)	Scrubber water flow rate (L/min) ^a	Compound mass emission rate (10^{-6} kg/hr)
2/22/86	3-3	Naphthalene	8,900	32.5	17,355
		Acenaphthalene	39,000		76,050
		Acenaphthene	69		135
		Fluorene	810		1,580
		Phenanthrene	17,000		33,150
		Anthracene	730		1,424
		Fluoranthene	12,000		23,400
		Pyrene	12,000		23,400
		Benzo(A)Anthracene	690		1,346
		Chrysene	850		1,658
		Benzo(B)Fluoranthene	960		1,872
		Benzo(K)Fluoranthene	440		858
		Benzo(A)Pyrene	1,800		3,510
		Indeno(123-CD) Pyrene	1,700		3,315
		Benzo(GHI)Perylene	5,400		10,530
		2-methylnaphthalene	100		195

^aScrubber water flowrate obtained from PSI via NYSDEC.

PCBs, Chlorobenzenes, PCDDs/PCDFs--

Split scrubber water samples were analyzed by Zenon Environmental, Inc. for PCB, PCDD, and PCDF content. In addition, Run 3-1 scrubber water samples were analyzed for chlorobenzenes, chlorophenols, and benzo (a) pyrene. The resultant data from these analyses are given in Table 2-10. The concentrations given are combined aqueous and carbon phase concentrations of each compound. As can be seen from the data in Table 2-10, PCDDs were not detected in the scrubber water in any of the runs. PCDFs were detected in only the first run and mono through decachlorinated biphenyls in the last two runs. It should be noted that mono and dichlorinated biphenyls represent approximately 89 and 81 percent of the total PCB mass in Runs 3-2 and 3-3, respectively.

Postflare Stack Gas

Stack gas samples were collected during each run utilizing a variety of sampling trains and methods to obtain the required parameters. The stack gas constituents sampled for included O₂, CO₂, CO, NO_x, particulate matter, HCl, volatiles, semivolatiles, PCBs, and PCDDs/PCDFs. Also included were measurements of gas temperature, velocity, and moisture. As stated earlier, Run 3-1 was limited to 115 minutes of sampling time due to a malfunction of the power supply to the torch. During the three test runs, some problems also arose with the sampling equipment due to the very cold weather causing sample lines and pumps to freeze. Extremely high temperatures within the stack created numerous problems especially during Run 3-2 when gas temperatures approached 1150°C (2100°F). Runs 3-2 and 3-3 were sampled to completion, however, for total run times of 240 minutes (4 hours) each. The test runs and resultant data are summarized and discussed in the following subsections.

Combustion Data--

During the three operational periods in which sampling runs 3-1, 3-2, and 3-3 were conducted, the postflare stack gas was monitored for O₂, CO₂, CO, and NO_x using GCA's continuous emission monitoring system (CEMS). These analyzers are frequently used in determining combustion efficiency for diagnostic purposes as well as for determining overall CO and/or NO_x emission rates for regulatory purposes. The emission rates are calculated using stack gas flow rates and the analyzers' responses in concentration (ppm-pollutant). The data are summarized and presented in Table 2-11 in conjunction with stack gas flow rates obtained during the semivolatile sampling via Modified Method 5 (MM5).

HCl--

Emissions of hydrochloric acid were sampled at the postflare stack to determine stack gas concentrations as well as the HCl mass emission rates. Concentrations in the gas stream were quite low during all three runs averaging only 1.68 mg/m³ for an average emission rate of 64.1 mg/min. or 0.0084 lb/hr. The data summary is presented in Table 2-12 with the particulate emission data.

TABLE 2-10. SCRUBBER WATER - CHLORINATED SPECIES MASS EMISSION RATES^a

Date	Run #	Compound	Concentration ($\mu\text{g/L}$)	Scrubber water flow rate (L/min) ^b	Compound mass emission rate (10^{-6} kg/hr)
2/12/86	3-1	Di-Pentachlorophenols	ND	36.5	NA
		Benzo(A) pyrene	329		720.1
		Tetra-Octachlorinated dibenzo dioxins	ND		NA
		Tetra-Octachlorinated dibenzo furans	0.00072		0.0016
		Dichlorobenzene	0.29		0.64
		Trichlorobenzene	0.20		0.44
		Mono-Decachlorinated biphenyls	ND		NA
2/20/86	3-2	Mono-decachlorinated biphenyls	47.0	33.0	93.1
		Tetra-Octachlorinated dibenzodioxins	ND		NA
		Tetra-Octachlorinated dibenzo furans	ND		NA
2/22/86	3-3	Mono-decachlorinated biphenyls	10.0	32.5	19.5
		Tetra-Octachlorinated dibenzo dioxins	ND		NA
		Tetra-Octachlorinated dibenzo furans	ND		NA

^a Analytical results from Zenon Environmental, Inc.^b Scrubber water flow rate obtained from PSI via NYSDEC.

TABLE 2-11. POSTFLARE STACK GAS COMBUSTION DATA - PCB TRIAL BURNS

Parameter	Run number			Average
	3-1	3-2	3-3	
Date	2/12/86	2/20/86	2/22/86	
Test Duration, min.	115	240	240	
Stack Gas Temperature, °C	576	907	871	785
°F	1,070	1,664	1,599	1,444
Stack Gas Velocity, m/sec	17.8	20.8	19.5	19.4
ft/min	3,511	4,090	3,843	3,814
Stack Gas Flow Rate, m ³ /min ^a	45.43	36.41	35.81	39.22
ft ³ /min ^a	1,604.0	1,285.6	1,264.4	1,384.7
Oxygen, percent	15.8	14.0	15.3	15.0
Carbon Dioxide, percent	3.8	5.1	4.3	4.4
Carbon Monoxide, ppm	18	20	20	19
kg/hr	0.057	0.051	0.050	0.053
lb/hr	0.126	0.112	0.110	0.116
Oxides of Nitrogen, ppm	96	115	108	106
kg/hr	0.502	0.482	0.445	0.476
lb/hr	1.104	1.060	0.979	1.048

^aDry standard conditions defined as 20°C and 760 mm Hg.

Particulate Matter--

Prior to analyzing the MM5 filters and probe rinses for semivolatile compounds, the particulate catch was weighed and used in calculating particulate emissions from the stack. The results of the three test runs show an average particulate concentration of 0.005 grains per dry standard cubic foot (gr/dscf) with an average emission rate of 463.2 mg/min or 0.061 lb/hr. Run 3-1 results were almost twice as high as those from Run 3-2 or 3-3. During run 3-1, the stack gas temperature was much lower and the stack gas flow rate was higher than the two subsequent runs. The system problems which led to a shortening of the test period may also have caused the increased grain loading (i.e., higher carbon concentrations in the reactor gas and postflare stack gas). The data from the three test periods are compiled in Table 2-12 along with HCl emission data.

Volatile Organic Compounds--

The postflare stack gas was sampled for volatile organic compounds (VOCs) using a Volatile Organic Sampling Train (VOST). The results of the sampling are not available because the holding times of the samples and the upper temperature limits for storage were exceeded. The results of the analyses would be deemed erroneous because it is unclear what the breakdown components would be after the samples were allowed to become warm. Extrapolating from the data obtained from the scrubber water analyses, the most prevalent constituents in the preflare product gas could be primarily benzene, chlorobenzene, toluene (methylbenzene) and styrene (ethenylbenzene) with boiling points ranging from 80 to 110°C. It is estimated that in the postflare stack gas, only the higher boiling compounds would be present (i.e., styrene). However, as the PCB concentrations in the stack gas were not detectable, it may be that the more volatile species would not have withstood the 900°C stack temperatures and thus, not have been detected.

Semivolatile Organic Compounds--

Sampling for semivolatile organics took place during each test period using a Modified Method 5 (MM5) sampling train with an XAD sorbent module in place. Coincident with this sampling was another similar train used for the collection of semivolatile organics solely for analysis for PCBs, PCDDs, and PCDFs.

The semivolatile samples were analyzed by GCA's laboratory utilizing GC/MS. As with the scrubber water samples, the principal components found were naphthalene and its sister compounds. The various concentrations and resultant emission rates are shown on Table 2-13. The sampling and analytical methods are described in Sections 5 and 6, respectively.

Chlorinated Species - PCBs, PCDDs, and PCDFs--

A sampling train similar to the one used for the collection of nonchlorinated semivolatile organic compounds was used to collect chlorinated samples to be analyzed for polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). These samples were delivered to Zenon Environmental, Inc. for subsequent analysis following each test run. The resultant data from the three test runs are presented in Table 2-14. A destruction and removal efficiency (DRE) for the

TABLE 2-12. POSTFLARE STACK GAS PARTICULATE AND HCl EMISSIONS DATA

Parameter	Run number			Average
	3-1	3-2	3-3	
Date	2/12/86	2/20/86	2/22/86	
Test duration, min.	115	240	240	
Stack Gas Flow Rate, m ³ /min ^a ft ³ /min ^a	45.43 1,604.0	36.41 1,285.6	35.81 1,264.4	39.22 1,384.7
Stack Gas Temperature, °C °F	576 1,070	907 1,664	871 1,599	785 1,444
<u>Particulate Matter</u>				
Concentration, gr/dscf mg/m ³	0.00692 15.84	0.00332 7.60	0.00479 10.96	0.00500 11.47
Emission Rate, mg/min kg/hr	720.0 0.043	276.6 0.017	393.0 0.024	463.2 0.028
<u>HCl</u>				
Concentration, mg/m ^{3b}	1.07	2.68	1.29	1.68
Emission Rate, mg/min ^b kg/hr ^b lb/hr ^b	48.3 0.0029 0.0063	97.8 0.0059 0.0129	46.3 0.0028 0.0061	64.1 0.0039 0.0084

^aDry standard conditions as defined by 20°C and 760 mm Hg.

^bHCl Concentrations and Emission Rates during Run 3-1 are the results of 1 test during the test run. Data from Runs 3-2 and 3-3 are averages of 3 tests during each test run.

TABLE 2-13. POST-FLARE STACK GAS - SEMIVOLATILE MASS EMISSION RATES^a

Date	Run #	Compound	Concentration ($\mu\text{g}/\text{m}^3$)	Stack gas flow rate (m^3/min)	Compound Mass (lb/hr)	Emission Rate (mg/min)
2/12/86	3-1	Naphthalene	46.40	45.43	27.88x10 ⁻⁵	2.11
		Acenaphthalene	37.96		22.81	1.72
		Phenanthrene	50.62		30.42	2.30
		Fluoranthene	21.09		12.67	0.96
		Pyrene	7.59		4.56	0.34
		2-Methylnaphthalene	6.33		3.80	0.29
2/20/86	3-2	2-Methyphenol	8.59		4.56	0.34
		Naphthalene	244.42	36.41	117.71	8.90
		Acenaphthalene	8.65		4.17	0.32
		Phenanthrene	63.92		30.79	2.33
		2-Methylnaphthalene	30.08		14.49	1.10
		Dibenzofuran	28.20		13.58	1.03
2/21/86	3-3	Naphthalene	8.92	35.81	4.22	0.32
		Acenaphthalene	1.55		0.73	0.06
		Phenanthrene	8.14		3.92	0.30
		2-Methylnaphthalene	1.36		0.64	0.05
		Dibenzofuran	1.74		0.83	0.06

^a Does not include PCB, PCDD/PCDF mass emission rates - see Table 2-14.

TABLE 2-14. POST-FLARE STACK GAS - CHLORINATED SEMIVOLATILE ORGANIC COMPOUND MASS EMISSION RATE^a

Date	Run #	Compound	Concentration (ng/m ³)	Stack gas flow rate (m ³ /min)	Compound mass emission rate	
					(mg/min)	(10 ⁻⁶ kg/hr)
2/12/86	3-1	Dichlorophenol	88.9	44.69	0.004	0.24
		Trichlorophenol	164.1		0.007	0.44
		Tetrachlorophenol	74.8		0.003	0.20
		Pentachlorophenol	244.0		0.011	0.65
		Dichlorobenzene	495.0		0.022	1.32
		Trichlorobenzene	385.9		0.017	1.03
		Tetrachlorobenzene	233.9		0.010	0.63
		Pentachlorobenzene	424.8		0.019	1.14
		Dichlorinated biphenyl	39.0		0.002	0.10
		Trichlorinated biphenyl	2.7		0.0001	0.01
		Mono-decachlorinated biphenyl	41.7		0.002	0.11
		Hexachlorinated dibenzodioxin	1.4		6.3x10 ⁻⁵	0.004
		Heptachlorinated dibenzodioxin	2.0		8.9x10 ⁻⁵	0.005
		Octachlorinated dibenzodioxin	0.6		2.7x10 ⁻⁵	0.002
		Hexa-octachlorinated dibenzodioxin ^b	4.0		17.9x10 ⁻⁵	0.011
		Tetrachlorinated dibenzofuran	25.7		114.9x10 ⁻⁵	0.069
		Pentachlorinated dibenzofuran	26.0		116.2x10 ⁻⁵	0.070
		Hexachlorinated dibenzofuran	21.8		97.4x10 ⁻⁵	0.058
		Heptachlorinated dibenzofuran	9.6		42.9x10 ⁻⁵	0.026
		Octachlorinated dibenzofuran	6.5		29.0x10 ⁻⁵	0.017
		Tetra-octachlorinated dibenzofuran	89.6		400.4x10 ⁻⁵	0.240

(continued)

TABLE 2-14 (continued)

Date	Run #	Compound	Concentration (ng/m ³)	Stack gas flow rate (m ³ /min)	Compound mass emission rate	
					(mg/min)	(10 ⁻⁶ kg/hr)
2/20/86	3-2	Mono-decachlorinated biphenyl	ND	36.46	NA	NA
		Pentachlorinated dibenzodioxin	0.2		0.7x10 ⁻⁵	0.0004
		Hexachlorinated dibenzodioxin	2.1		7.7x10 ⁻⁵	0.005
		Heptachlorinated dibenzodioxin	4.8		17.5x10 ⁻⁵	0.011
		Octachlorinated dibenzodioxin	5.6		20.4x10 ⁻⁵	0.012
		Penta-octachlorinated dibenzodioxin ^b	12.6		45.9x10 ⁻⁵	0.028
		Tetrachlorinated dibenzofuran	12.0		43.8x10 ⁻⁵	0.026
		Pentachlorinated dibenzofuran	18.1		66.0x10 ⁻⁵	0.040
		Hexachlorinated dibenzofuran	26.1		95.2x10 ⁻⁵	0.057
		Heptachlorinated dibenzofuran	39.5		144.0x10 ⁻⁵	0.086
		Octachlorinated dibenzofuran	43.1		157.1x10 ⁻⁵	0.094
		Tetra-octachlorinated dibenzofuran	138.8		506.1x10 ⁻⁵	0.304

(continued)

TABLE 2-14 (continued)

Date	Run #	Compound	Concentration (ng/m ³)	Stack gas flow rate (m ³ /min)	Compound mass emission rate	
					(mg/min)	(10 ⁻⁶ kg/hr)
2/22/86	3-3	Mono-decachlorinated biphenyl	ND	34.95	NA	NA
		Penta-octachlorinated dibenzodioxin ^b	ND		NA	NA
		Tetrachlorinated dibenzofuran	4.5		15.7x10 ⁻⁵	0.009
		Pentachlorinated dibenzofuran	7.6		26.6x10 ⁻⁵	0.016
		Hexachlorinated dibenzofuran	7.2		25.2x10 ⁻⁵	0.015
		Heptachlorinated dibenzofuran	11.1		38.8x10 ⁻⁵	0.023
		Octachlorinated dibenzofuran	8.8		30.8x10 ⁻⁵	0.018
		Tetra-octachlorinated dibenzofuran	39.1		136.7x10 ⁻⁵	0.082

^aAnalytical data from report received from Zenon Environmental, Inc. via Drs. Hugh Dibbs (EPS) and Thomas Barton (PSI).

^bTetrachlorinated dibenzodioxin not detected in all three runs.

plasma pyrolysis system when firing PCB-containing liquid wastes was also calculated for each run and is presented in Table 2-15. Sampling and analytical methods are described in Sections 5 and 6, respectively.

In calculating the DRE for PCBs during Runs 3-2, and 3-3, an estimate of the maximum possible PCB emission rate had to be used for these runs because the sample analyses yielded results below the instrument detection limits. This estimate uses the sum of the minimum detection limits for mono through decachlorinated biphenyls. It is expected that the actual PCB emission rate is far below that calculated using the minimum detection limits. The emission rate values are therefore preceded by a "less than" symbol to signify that the value given is a maximum possible emission rate. Therefore, the calculated DREs from Runs 3-2 and 3-3 may not be representative of actual conditions but serve to provide an absolute minimum destruction/removal efficiency value. The calculations used in this determination are as follows:

	PCB Congener									
	Cl-1	Cl-2	Cl-3	Cl-4	Cl-5	Cl-6	Cl-7	Cl-8	Cl-9	Cl-10
Detection limit* (total ng)	2	2	2	2	2	2	4	4	4	4

Sum of Detection Limits (Cl-1 - Cl-10 PCB) 28 ng

Therefore,

Run 3-2

$$\frac{28 \text{ ng}}{5.54 \text{ m}^3} \times \frac{36.46 \text{ m}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{\text{kg}}{1 \times 10^{12} \text{ ng}} = 1.1 \times 10^{-8} \text{ kg/hr}$$

Run 3-3

$$\frac{28 \text{ ng}}{5.14 \text{ m}^3} \times \frac{34.95 \text{ m}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{\text{kg}}{1 \times 10^{12} \text{ ng}} = 1.1 \times 10^{-8} \text{ kg/hr}$$

Where: 36.46 m³/min = Volumetric flow rate of stack gas during Run 3-2.
 34.95 m³/min = Volumetric flow rate of stack gas during Run 3-3.
 5.54 m³ = Volume sampled by MM5 train during Run 3-2.
 5.14 m³ = Volume sampled by MM5 train during Run 3-3.

*Detection limit data obtained from Zenon Environmental, Inc.

TABLE 2-15. PLASMA PYROLYSIS SYSTEM DRE FOR PCBs^a IN A LIQUID WASTE FEED

Date	Run #	Run duration (min)	Waste feed rate (kg/min)	PCB content (% weight)	PCB mass input (kg/hr)	PCB mass out (kg/hr) ^b	System DRE percent
2/12/86	3-1	115	2.10	14.3	18.018	0.11x10 ⁻⁶	>99.9999
2/20/86	3-2	240	2.33	12.5	17.475	<1.1x10 ^{-8c}	>99.9999
2/22/86	3-3	240	2.20	12.8	16.896	<1.1x10 ^{-8c}	>99.9999

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^aTotal PCBs as mono (1) through deca (10) polychlorinated biphenyls.^bPCB mass out does not include PCB mass discharged through scrubber water. Only stack emissions are used in the calculations.^cConcentrations of PCBs were below the instrument detection limits according to Zenon's analyses.

In order to establish a minimum DRE, the sum of their detection limits for Cl-1 - Cl-10 was used to obtain a maximum possible emission rate.

CONCLUSIONS

Based on the test results and the operational experience associated with this test program, several conclusions can be drawn. First and foremost, the technology should be treated as a promising emerging technology which should be further demonstrated during subsequent trial burn programs.

The notable conclusions which are drawn from the test program are summarized below. These conclusions are focused on the demonstration of an acceptable destruction and removal efficiency as delineated in the RCRA and TSCA regulations.

- Results from the carbon tetrachloride test burns indicate that the system is capable of destroying a "difficult to destroy" RCRA regulated waste. The DREs from each of the three test burns exceeded the minimum RCRA requirement of ≥ 99.99 percent destruction removal efficiency.
- HCl emission rates conformed to the allowable limits of ≤ 4 kg/hr and ≥ 99 percent removal efficiency based on total inlet chlorine content.
- Concentrations of CCl_4 in the scrubber effluent ranged from 1.27-5.47 $\mu\text{g/L}$. Effluent levels met the criteria for discharge to the sewage treatment plant.
- Results from the PCB test burns indicate that the system is capable of destroying a PCB liquid waste blend consistent with the TSCA requirement of ≥ 99.9999 percent DRE.
- HCl emission rates were again consistent with the requirement of ≥ 99 percent removal efficiency and ≤ 4 kg/hr emission rate based on the chlorine input.
- High concentrations of polynuclear aromatic hydrocarbon compounds were detected in the two-phased scrubber effluent. The predominant species were naphthalene, acenaphthalene, phenanthrene, pyrene, and fluoranthene. Levels were in the range of 12,000-72,000 $\mu\text{g/L}$. Corresponding levels in the flue gas discharge were less than 245 $\mu\text{g/m}^3$.
- No appreciable levels of dioxin or furan compounds (as total tetra through octa) were detected in the scrubber water. In all cases, levels were either nondetectable or significantly less than 1 ng/L. Corresponding levels in the flue gas were in the range of 39 - 139 ng/ m^3 for the total tetra-octachlorinated dibenzofuran compounds and ND - 12.6 ng/ m^3 for the tetra-octachlorinated dibenzo-p-dioxin compounds.

SECTION 3

FACILITY DESCRIPTION

The mobile plasma pyrolysis system, operated by Pyrolysis Systems, Inc., was tested while located on the grounds of the Royal Military College in Kingston, Ontario, Canada. The major portion of the system was contained within a 45 foot, specially adapted trailer, capable of being transported from site to site. Ancillary equipment, such as the power transformer, waste feed blending area, and limited waste storage facilities were located in a secure, contained area within adjacent Building 62. The flare and postflare stack were located on the opposite side of the trailer from the building in a fairly open area (Figure 3-1).

PROCESS DESCRIPTION

The PSI plasma pyrolysis process is based on the concept of reducing (pyrolyzing) waste molecules to the atomic state using a thermal plasma field. A co-linear electrode assembly is used to produce the electric arc. Dried, low pressure air is used as the medium through which the electric current passes. Air molecules are subsequently ionized forming the plasma field. Upon return to the ground state, the ionized molecules emit ultraviolet radiation.

Hazardous waste mixtures are injected into the field and interact with the plasma field. This interaction results in a reducing mechanism in which the molecules are atomized. Upon cooling, simpler molecules such as hydrogen, carbon dioxide, carbon monoxide, hydrogen chloride and other minor matrix compounds such as acetylene and ethene are formed.

PSI operated the plasma system and the online analytical equipment. The online system generated composition data associated with the product gas (prior to flaring operations). PSI was also responsible for providing and preparing synthetic waste feed blends for subsequent testing. These test blends were identified in the PSI Quality Assurance test plan.

Figure 3-2 shows a block diagram of the plasma pyrolysis unit which is the focus of this program. The system consists of a liquid waste feed system, pyrolysis reactor, caustic scrubber, flare and online analytical equipment.

Gaseous effluents from the reactor pass through a caustic venturi type scrubber where acid gas removal is effected. Scrubber water discharge is on the order of 32 liters per minute. Subsequently, the product gas is flared to

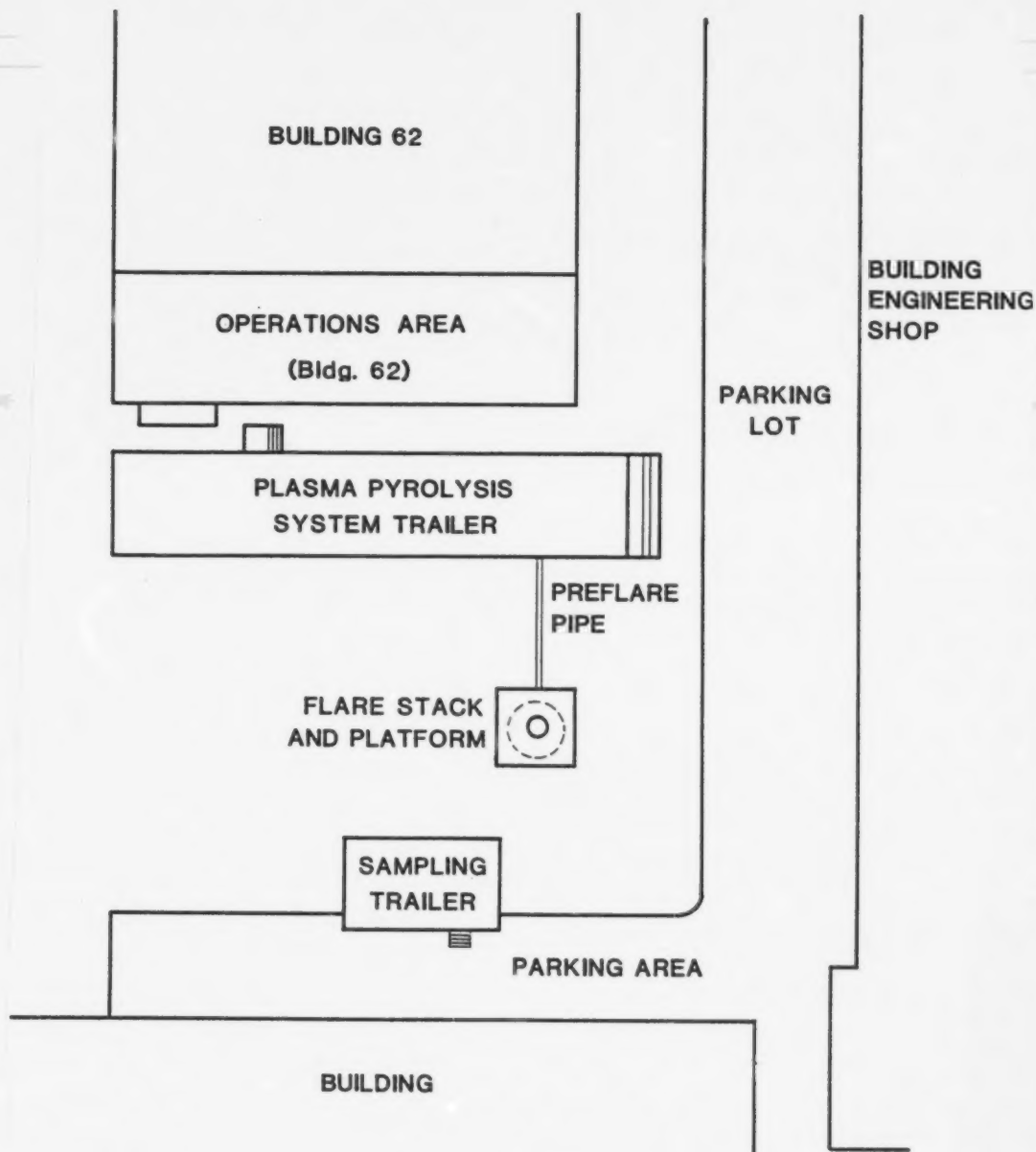
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Figure 3-1. Facility area top view.

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FLOW DIAGRAM

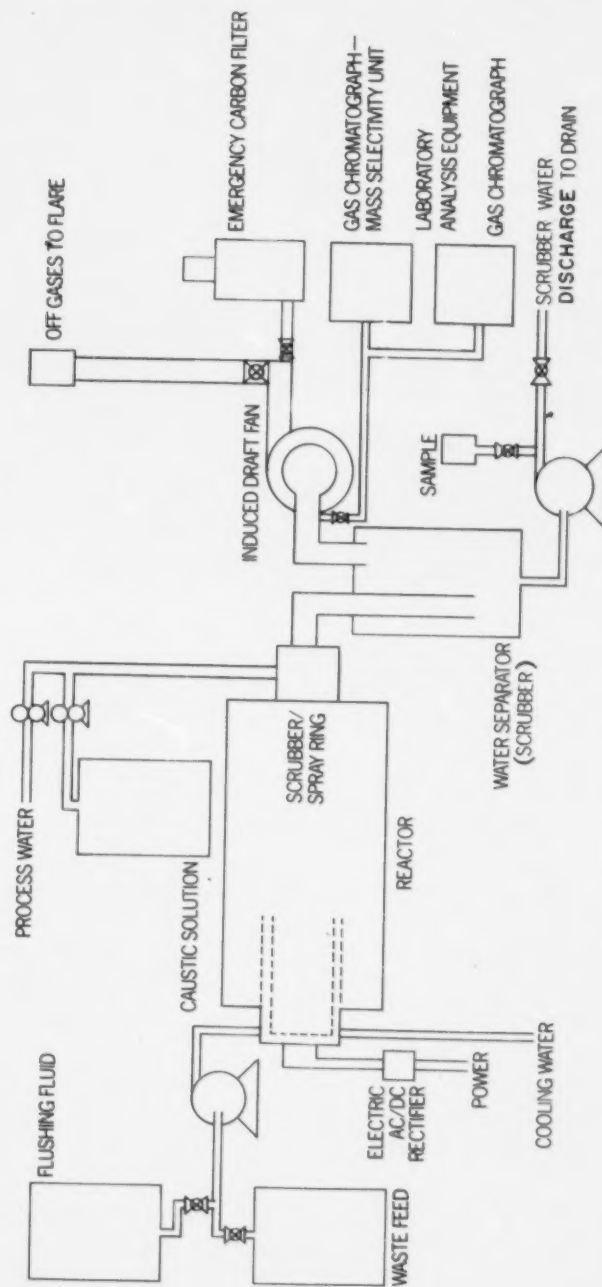


Figure 3-2. Process schematic of the PSI plasma pyrolysis unit.
(from Pyrolysis Systems, Inc.)

complete the cleanup cycle. The post flare gas then enters the stack and is discharged at the approximate height of 8 meters above grade.

The nominal treatment capacity of the system is 4 kg/min of waste feed or approximately 200 L/hr. Product gas production rates at this operating level are on the order of 5-6 m³/min prior to flaring operations.

For the purposes of this test program, a flare containment chamber and a stack were included to facilitate testing. After combustion, the flue gas flow rate was on the order of 36 m³/min at standard conditions.

SECTION 4

SAMPLING LOCATIONS

The locations for collecting the various sample types are shown in Figure 4-1. The locations remained unchanged from the original Quality Assurance Project Plan with one exception. At the preflare product gas sampling location, difficulty was encountered in obtaining representative samples due to very high carbon loading and entrained moisture. Additionally, during several system upsets, hydrogen flarebacks occurred creating a safety hazard at that location and caused sample probes to be blown out of the port. No further testing took place at that location.

WASTE FEED

The waste feed was sampled downstream of the blending and pumping operations through a valve assembly just prior to entering the reactor feed ring (Figure 4-2). The feed line was under pressure thus enabling an integrated waste feed sample to be obtained during each test run.

REACTOR ASH

Reactor ash was sampled from the interior of the reactor. Because the entire torch assembly, cooling water jacket feed ring, and graphite core had to be removed to accomplish this, ash samples were taken only when available.

SCRUBBER WATER

Scrubber water samples were obtained at the discharge point of the drain hose as shown previously in Figure 4-1.

POSTFLARE PRODUCT GAS

The stack is constructed of 1/4 inch stainless steel plate rolled to an I.D. of 16 inches. The flare containment vessel is similarly constructed, but with a 48 inch to a 16 inch I.D. taper, beginning approximately 21 inches from the base. The flare head, constructed of a 4 inch stainless steel elbow, protrudes into the containment vessel where the reactor product gases are ignited. The flare is self-sustaining and could be ignited either remotely with an ignitor fixed in place, or manually, by placing the ignitor into position until the flare was lit and then withdrawing it. It was found that the latter was the more reliable as the ignitor was not continually subjected to the vibration and extreme heat present at the flare head.

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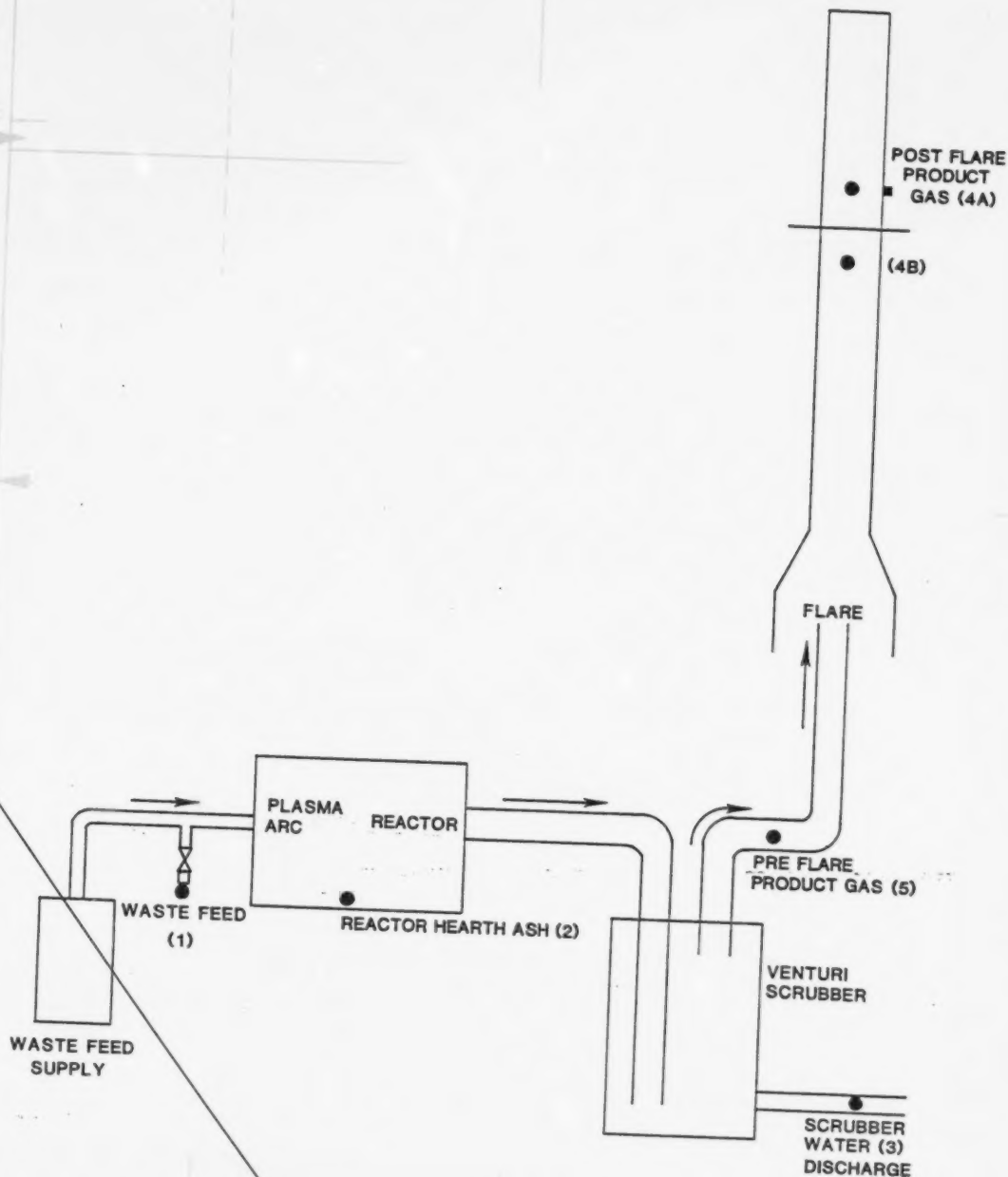


Figure 4-1. Plasma pyrolysis system flow diagram (abbreviated to only show sampling locations).

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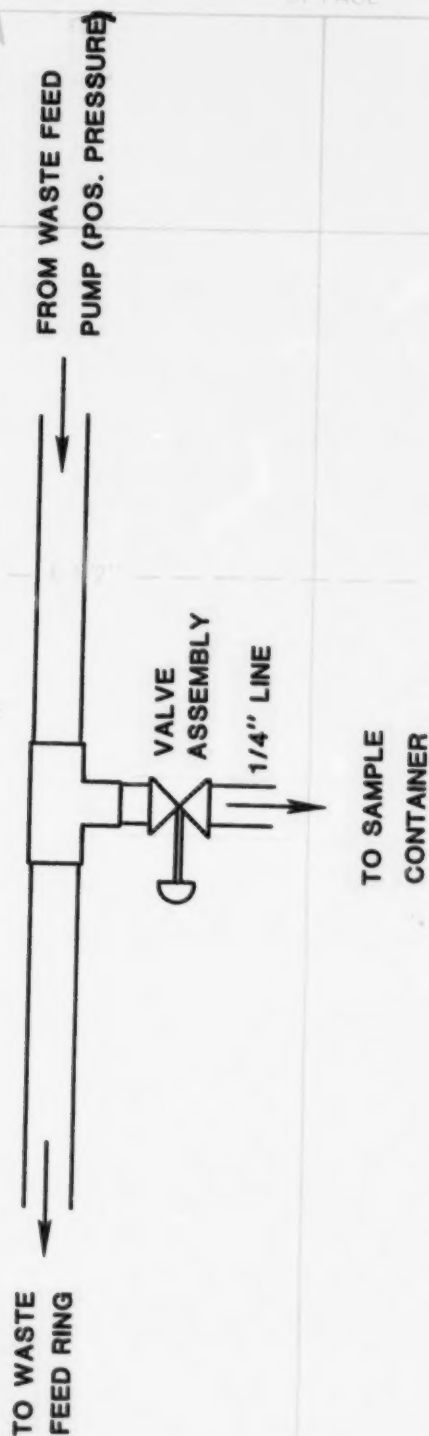
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Figure 4-2. Waste feed sampling location.

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The flare stack was designed with the flare containment vessel to allow for the rapid expansion of the combusted reactor product gas. The vessel is open at the base with an opening area of 1.17 square meters (12.56 ft²). This opening, in conjunction with the rapidly heated gases, allows for a flame and stack gas buoyancy which eliminates the need for induced draft or forced draft fan. In spite of the lack of a fan, once the flare is lit and temperatures have stabilized somewhat, the gas flow rates through the stack are also relatively stable. There is the presence of temperature spikes at times which is usually attributed to re-entrained carbon at the flare head or changing hydrogen content of the reactor product gas.

Postflare product gas samples were taken from two locations downstream of the flare. The flow diagram in Figure 4-1 shows these locations in relation to the rest of the process. Figure 4-3 illustrates the postflare stack configuration and sampling port locations with their associated measurements. It should be noted that, although the sampling location for the MM5 trains satisfied the 8/2 criteria for laminar flow, the small diameter of the stack (16 inches), in conjunction with the number and types of sampling probes required for the program, is not conducive to obtaining accurate flow measurements. The high temperatures found in the stack necessitated the use of water cooled probes for the MM5 trains. Two MM5 trains were required by the Administrator to be run simultaneously in order to provide separate PCB/Dioxin and semivolatile samples. The blockage caused by these probes alone approaches 22 percent. Further flow disturbances within the stack could have been caused by the other in-stack probes situated 72 inches upstream of the water cooled probes. However, in spite of the blockage and possible flow disturbances, the velocities and flow rates measured by both trains during all three test runs were in close agreement (within 5 percent). The sampling points for all trains are illustrated in Figure 4-4.

The HCl and VOST sample probes were located 3.78 diameters downstream of the flare containment vessel. During the CCl₄ burns, the CEM probe and filter were colocated with the HCl probe, as there were no VOST runs required during Stage II, Test Series 1. The CCl₄ integrated bag sampling systems were set up on the sampling platform and sampling was conducted from one of the upper ports.

During Test Series 3, the two MM5 trains, as well as the CEM probe and filter hotbox, were set up at the upper ports, 8.28 diameters downstream of the flare containment vessel. The CEM probe was bent at a 45 degree angle in order to eliminate interference with the MM5 sampling probe in port A. The CEM probe tip remained on the same horizontal plan as the MM5 nozzles.

PREFLARE PRODUCT GAS

As mentioned earlier, sampling efforts at this location were aborted due to unsafe sampling conditions and very high carbon loading and entrained moisture. The stainless steel preflare pipe exits the trailer approximately eight (8) feet off the ground, takes a downward bend, and then runs along the ground approximately twenty (20) feet before taking a 90° upward bend to form

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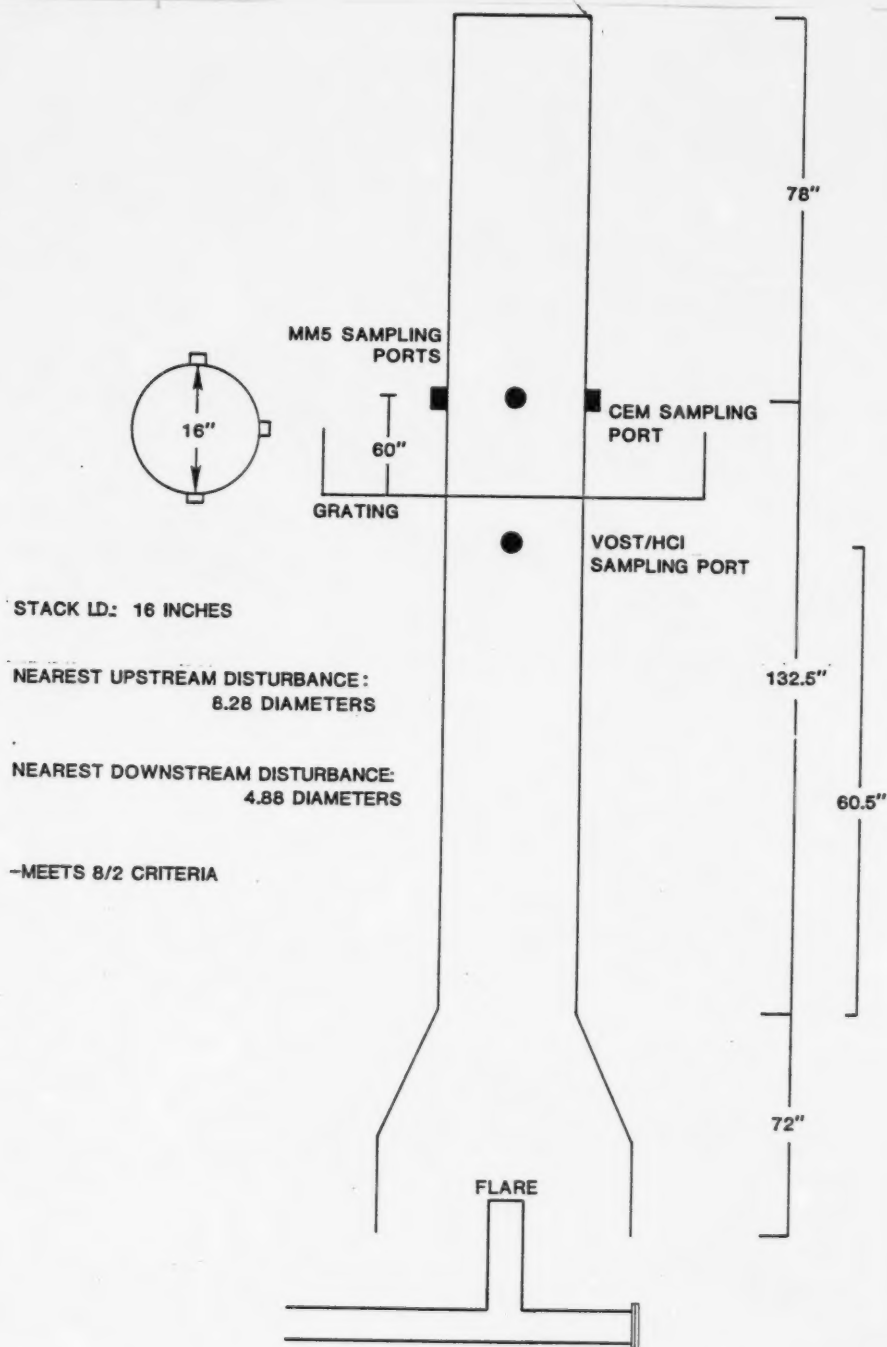


Figure 4-3. Postflare emission sampling locations.

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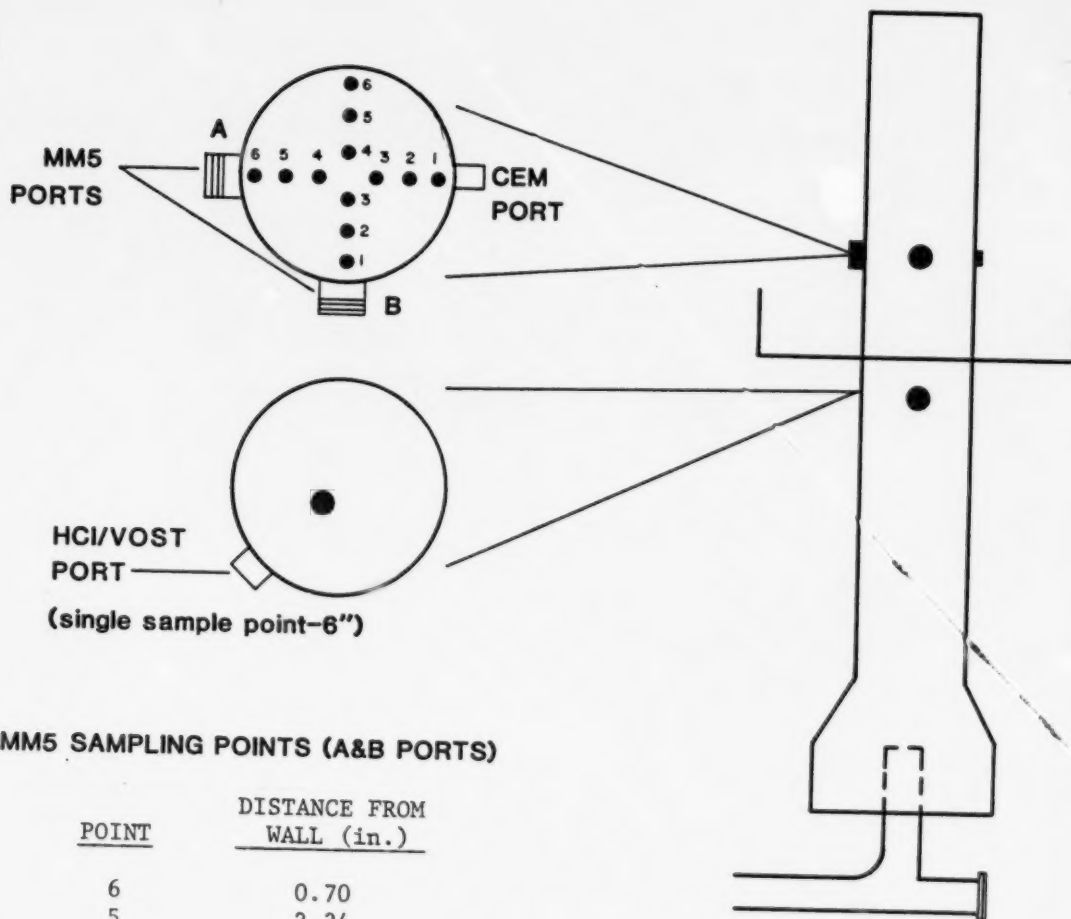


Figure 4-4. Sampling point locations.

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the flare. The ignitor was originally a permanently mounted spark source, but has since been altered so that it has to be manually put into place and removed during the ignition sequence. The preflare sample ports were located 90° to each other in the 6 inch stainless steel pipe approximately ten feet upstream of the flare. The heavy, moist carbon present in the preflare product gas caused plugging of the sampling equipment. It was theorized that, at times, some of the carbon buildup would break loose which would then hit the flare, possibly causing it to blow out. A 'T' connection was installed, replacing the original flare tip. The new 'T' acted as a settling point for some of the carbon instead of letting all of it pass through the flare. This can be seen in Figure 4-3.

SECTION 5

SAMPLING PROCEDURES

The procedures for obtaining samples of the waste feed, reactor ash, scrubber water, and postflare stack gas are described in this section. The methods used in sampling remained essentially unchanged from those described in the Quality Assurance Project Plan submitted for this program. Any deviations from the described methods are called out in Section 7. All containers used in collecting and/or storing these samples were prepared as stated in the QAPP. A summary of the sampling methods used follows.

WASTE FEED

Liquid wastes entering the plasma arc reactor enter by way of a machined waste feed ring. The waste feed is pumped from the drums in which it is blended, through the calibrated rotameter, through the stator pump, and into the waste feed ring. Just prior to the feed ring is a 'T' connection and valve assembly which allows a sample to be taken under positive pressure. The valve allows fine adjustment of the liquid flow so that an integrated sample can be taken over the duration of the test run. Waste feed sampling commenced after the system was switched over to the desired waste feed (i.e., CCl_4 or PCB, depending on the burn schedule). This ensured sampling only the target waste feed and not the flushing solvent blend (i.e., MEK/MEOH). If a system upset occurred during the sampling run, necessitating switching off the target waste feed, the sample valve was closed and not reopened until the target waste feed was switched back on and it was felt that sufficient volume had passed through to diminish any effects of dilution by the flushing solvent blend. At the end of each test run, the waste feed samples were returned to a waste feed drum after obtaining the required aliquots of the liquid which were then transported to Zenon Environmental, Inc. for subsequent analyses. GCA also archived waste feed samples from each test run.

REACTOR HEARTH ASH

Ash samples were not taken and analyzed by GCA. Some samples of carbon found deposited on the snow around the stack area were collected for NYSDEC to be analyzed by their laboratory. Also, samples of carbon were taken from inside the preflare gas pipe and relinquished to NYSDEC for analysis by their laboratory. The carbon samples were collected in wide mouth jars or 40 mL VOA vials, as appropriate. They were scooped into the containers using hexane rinsed stainless steel spatulas.

SCRUBBER WATER

The scrubber water samples were composited in a 10 liter jar every 30 minutes during each test run. During each grab sampling episode, two 40 mL VOA vials samples were taken for subsequent VOC analyses. A composite scrubber water sample for each run was collected for semivolatile analysis by the GCA laboratory. The 10 liter sample jars were transported to Zenon for analyses for PCBs and PCDDs/PCDFs. In all compositing efforts, the scrubber water was mixed thoroughly to ensure a representative carbon/aqueous solution mix. During some sampling periods, the amount of carbon present in the scrubber water was noticeably less than at other times.

POSTFLARE STACK GAS

Table 5-1 summarizes the sampling methodologies utilized in this program to characterize emissions from the pyrolysis system while pyrolyzing two types of chlorinated water feeds and flaring the product gas.

Bulk Gases

Continuous Monitoring--

A continuous monitoring system was in operation during the two test series of the project to monitor concentrations of CO, O₂, CO₂, and NO_x in the flue gas. In addition, continuous sensors for measuring postflare gas flow rates were included during the CCl₄ burns. An attempt to monitor flow rates and temperatures at the preflare location was aborted due to carbon plugging and the hydrogen flarebacks. The monitoring system was comprised of a gas conditioning system, for measuring CO, O₂, CO₂ and NO_x and a data acquisition system as shown in Figure 5-1.

The gas conditioning system consisted of a glass fiber filtration unit mounted on the probe to remove particulates and a condensate trap for primary moisture removal from the flue gas. The final step in moisture removal is achieved by an inline permeation drier. Sample gas exiting the permeation drier is then ready for analysis. Gas analyses will be performed using the instruments described in Table 5-2.

Carbon monoxide concentrations were measured using a Horiba Model PIR 2000 NDIR Analyzer in the operating range of 0 to 0.1 percent full scale. Calibrations preceded and succeeded each test by injecting the appropriate zero and span gases.

Oxygen concentrations were measured using a MSA Model 802 O₂ Analyzer in the operating range 0 to 25 percent full scale. The analyzer was calibrated before and after each test with a zero gas of ultrapure nitrogen and calibration span gases of the appropriate concentrations.

Carbon dioxide was measured using a Horiba PIR 2000 NDIR CO₂ Analyzer in the operating range 0 to 25 percent full scale. This analyzer was calibrated before and after each test with the applicable zero and span gases.

TABLE 5-1. PREFLARE AND POSTFLARE EMISSION PARAMETERS MEASUREMENTS

Parameter	Collection method
HCl	Impingers (TACB Method) ^a
Volatile Organics ^b	Integrated Tedlar Bag (onsite analyses for CCl ₄) Volatile Organic Sampling Train [(VOST) (offsite analyses)]
Semivolatiles	Modified Method 5 (MM5)
PCBs	Modified Method 5
PCDD/PCDF	Modified Method 5
Particulate matter	Modified Method 5

^aTexas Air Control Board Method.

^bBag sampling/onsite GC used for all 1-hour burns; VOST used during endurance burns.

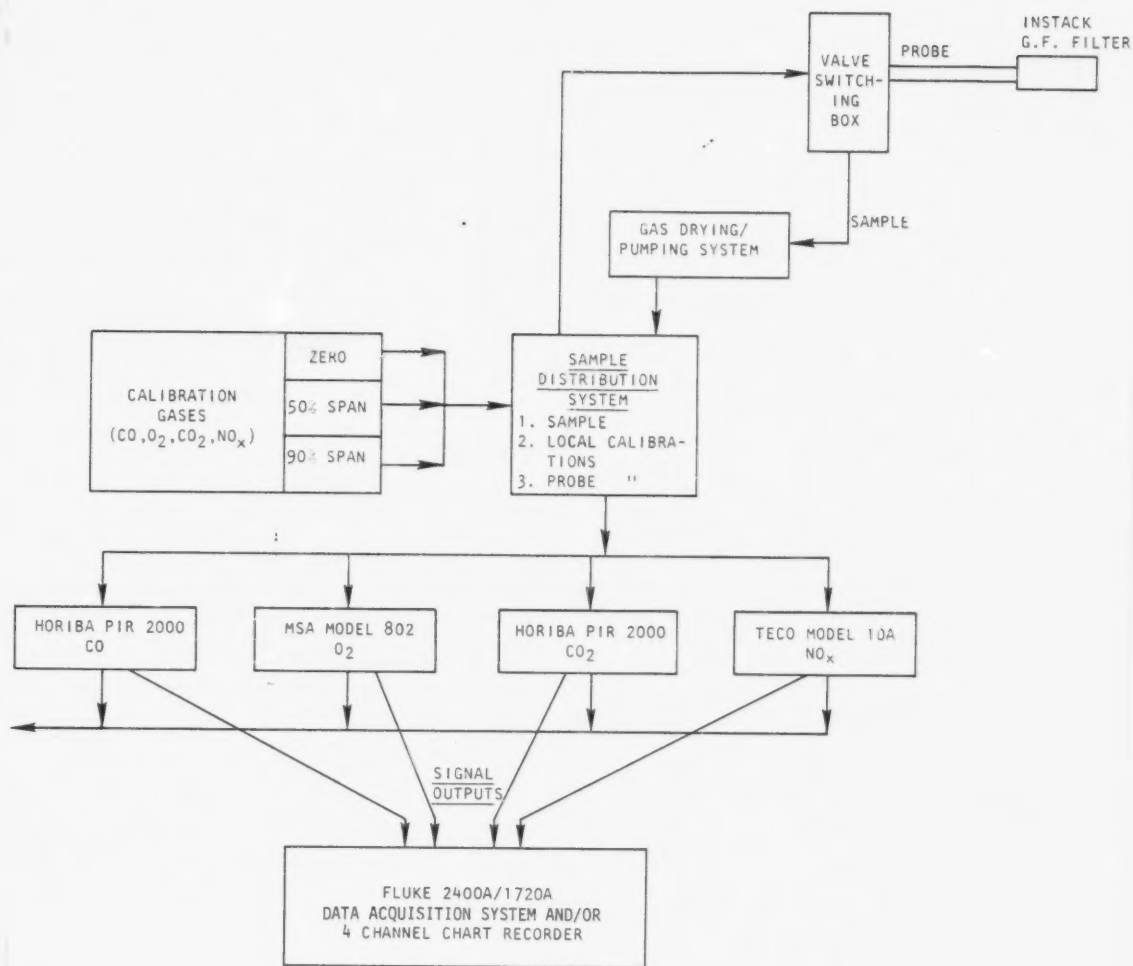


Figure 5-1. Continuous monitoring sampling schematic.

TABLE 5-2. CEM SAMPLING PARAMETERS AND METHODOLOGY

Parameter	Instrument model (detection)	Available measurement ranges (up to)
CO	Horiba PIR 2000 (NDIR)	5,000 ppm
O ₂	MSA Model 802 (Paramagnetic)	25%
CO ₂	Horiba PIR 2000 (NDIR)	25%
NO _x	TECO Model 10A (Chemiluminescence)	10,000 ppm
Velocity	Rosemont Instruments	5 inch W.C. P

Oxides of nitrogen (NO_x) were measured using a TECO Model 10AR Chemiluminescent NO_x Analyzer in the range of 0 to 1000 ppm. Calibration of the analyzer was accomplished using nitrogen zero gas and span gases of the appropriate concentrations.

Continuous monitoring of the flue gas was performed according to the following sequence:

1. Arrived onsite, inspected condition of equipment.
2. Set up and leak checked conditioning system through manifold.
3. Connected all four analyzers to the manifold and data acquisition system.
4. Performed initial calibration of all monitors with zero, mid and high span certified gases. Made any necessary adjustments on the monitors.
5. Monitored CO , O_2 , CO_2 and NO_x throughout the flue gas testing making sure to mark the strip charts noting the beginning and end of the test runs.
6. At the end of each run, recalibrated the monitors and noted all values on the appropriate data sheet to determine monitor drift.
7. Monitoring data were reduced and presented as average concentrations and, for CO and NO_x , hourly emission rates.

The continuous monitoring system inspection, installation and operation was performed in accordance with the applicable instrument manuals.

Flue Gas Molecular Weight by Integrated Orsat--

The flue gas molecular weight is required by TSCA and RCRA to be calculated from data representing each sampling point in the stack. Because the CEMS was situated for single-point monitoring, it was necessary to calculate the molecular weight from the average of the data from the four 1-hour integrated bag samples taken during each run. During Run 3-1, it was only possible to obtain two 1-hour samples due to the shortening of the test run. A lung sampling system was used to collect the integrated stack gas sample in a Tedlar bag. This system was leak-checked before and after each sampling run to ensure no leakage occurred during the run.

Trace Gases

The trace gas samples were collected from the postflare stack and were analyzed for HCl , semivolatiles, and, more specifically from the latter group, PCBs and PCDD/PCDF. Carbon tetrachloride and polychlorinated biphenyls were introduced into the plasma arc as separate waste matrices during the two test stages. The capability of the plasma arc system to either destroy or remove the target compounds were measured by the methods outlined in this subsection.

Volatile Organic Sampling Train (VOST)--

The VOST was used to collect VOCs present in the product flue gas during the long term endurance runs. VOC refers to those organic compounds with boiling points less than 150°C. The method utilizes Tenax and Tenax/Charcoal cartridges each of which is preceded by a condensing module to adsorb the VOCs.

The train consisted of a glass-lined probe with a glass wool plug to remove particulate, followed by an assembly of condensers and organic resin traps as illustrated in Figure 5-2. The first condenser cooled the gas stream and condensed the water vapor present. The flue gas and condensed moisture then passed through a cartridge containing 1.5 grams of Tenax resin (60-80 mesh). the condensate was collected in the first impinger which was continually purged by the gas stream. The second condenser and trap containing Tenax/charcoal served as a backup for low volume breakthrough compounds. Following the second Tenax trap is a silica gel drying tube for residual moisture removal. The sampling train was operated at a flow rate of 0.3 liters per minute and the total collection volume did not exceed 20 standard liters.

Sample temperature was monitored at the outlet of the sample probe and the inlet to the Tenax cartridge using thermocouples. The gas temperature through the probe was maintained above 150°C to prevent the premature condensation of the volatile components. The temperature of the gas through the resin cartridges was maintained at less than 20°C.

Extensive sorbent preparation and quality assurance procedures were instituted to ensure the integrity of these samples. All components of the system coming into contact with the samples were rinsed with DI water and dried in an oven at 150°C for a period of 2 hours prior to use. The Tenax adsorbent and glass wool packing were precleaned as described in the Quality Assurance Project Plan.

The presampling preparations for the VOST included:

- Washing the train and sample containers using the following sequence: soap and water, pre-extracted DDI water rinse, and methanol rinse.
- Preparing VOA vials for condensate recovery which were not solvent rinsed but were heated in an oven at 110°C for 2 hours.
- Setting up a field biased blank sampling train which was disassembled and recovered in the same manner as the actual VOST following each run.
- Collecting method blanks of DI water, Tenax, and charcoal.

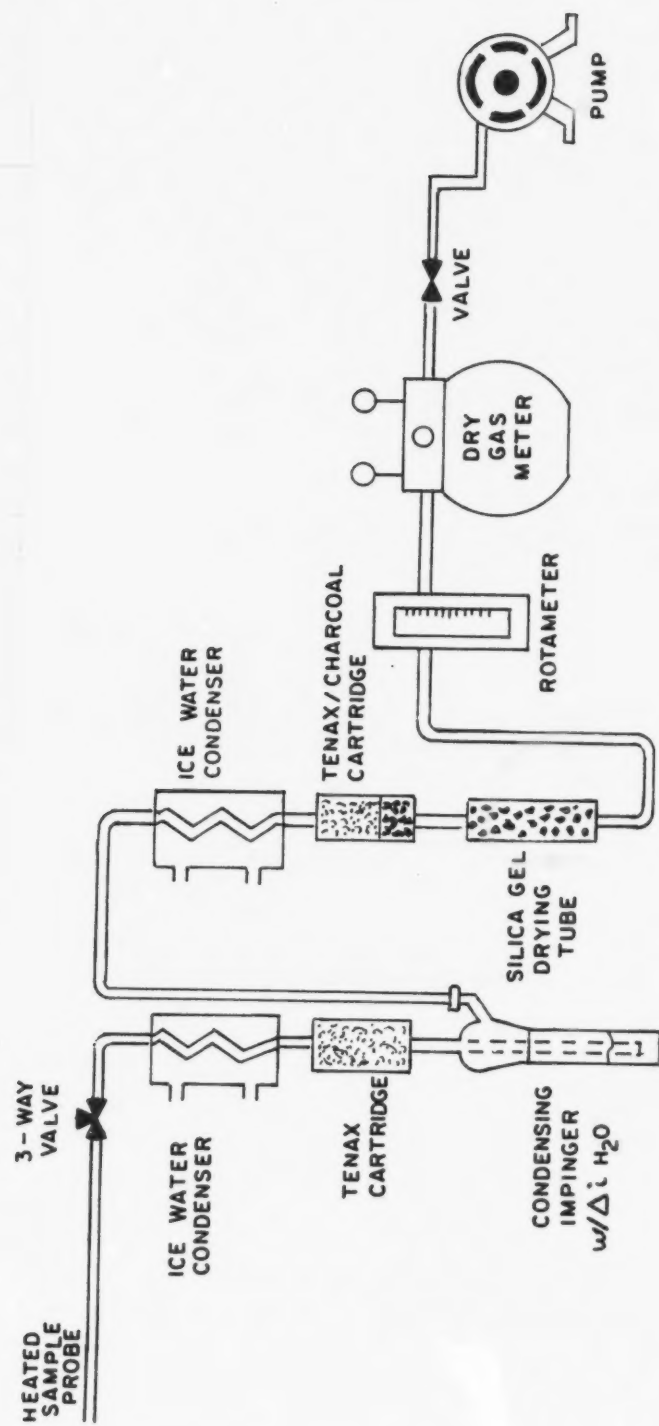


Figure 5-2. Volatile organic sampling train schematic.

The recovery activities for the VOST included:

- Removing VOST from stack and transporting to nearby recovery area.
- Sealing the sorbent cartridges with teflon tape and placing them in their original glass culture tubes with glass wool to absorb shock.
- Measuring the volume of the condensate impinger with a precleaned graduated cylinder.
- Transferring the measured condensate volume to 40 mL VOA vials and diluting to volume with DI water to decrease headspace and the possibility of revolatilization of the compounds.
- Further reducing reactivity by storing all samples at 4°C.

The samples which were collected during each VOST run consisted of a Tenax cartridge, a Tenax/charcoal cartridge, and the product gas condensate (captured by the mini impinger). All samples were labeled according to their series number, run number, sampling train type, sampling component, and parameter to be analyzed for.

Leak checks on the sampling train were performed before and after each sampling run. No portion of the trains were disassembled and reassembled during a test run. The sample train leak checks are documented on the field test data sheet for each respective run.

Integrated Bag Sampling for VOCs--

For the purpose of onsite analyses for the target volatile compounds during 1-hour CCl₄ burns, an integrated Tedlar bag collection method was utilized to collect the samples. A syringe was then used to draw a sample from the bag and inject onto the GC/ECD column.

The bag samples were collected on an hourly basis and analyzed for VOCs onsite by GC/ECD. One bag per day was filled with prepurified N₂ for use as a field-biased blank.

The gas bag sampling assembly employed is shown in Figure 5-3. It consisted of a cleaned, evacuated Tedlar bag placed inside a rigid container that was evacuated at a known rate during the sampling period. Prior to sampling, Tedlar bags were purged with prepurified nitrogen and evacuated. After the sample was drawn, a quick-disconnect valve atop the container sealed the sample in the bag for direct analysis.

Leak checks on the integrated bag sampling train were performed before and after each sampling run. The sample train leak checks and leakage rate (if applicable) are documented on the field test data sheet for each respective run.

Modified Method 5 (MM5)--

Modified Method 5 sampling trains were used for the collection of particulates, semivolatiles, polychlorinated biphenyls, and polychlorinated

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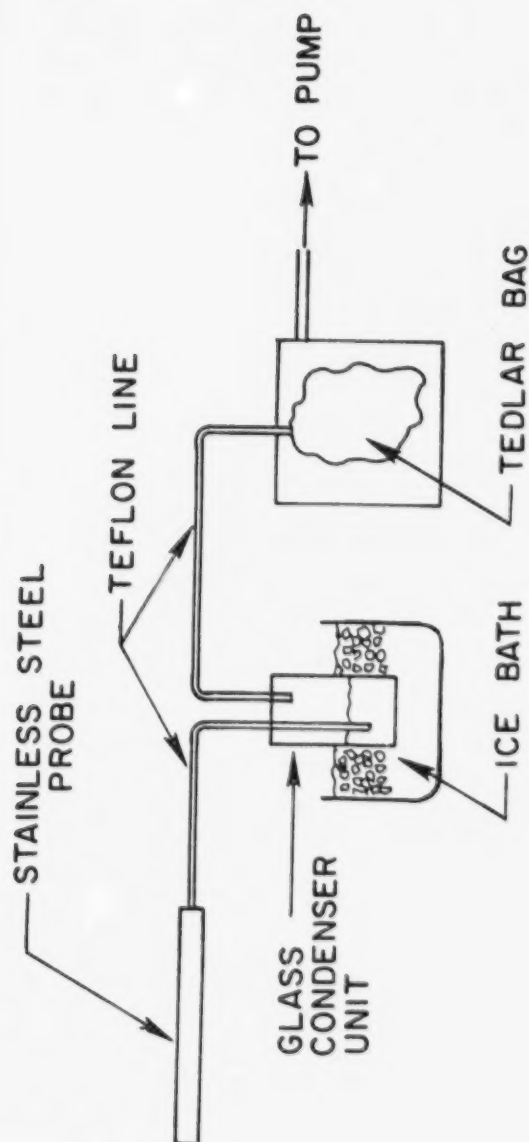


Figure 5-3. Integrated gas sampling train.

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dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/PCDF). A schematic of the MM5 sampling train is shown in Figure 5-4.

Additionally, a field-biased blank was set up at the site for each parameter (i.e., one semivolatile field blank, one PCB field blank) during each test day. It was set up and recovered exactly the same way as the actual sample but without having had sample gas flow through the system. The field-biased blanks were treated analytically the same way as actual samples and the results will provided appropriate blank corrections.

The sample train consisted of quartz glass-lined heat-traced water-cooled probe with an inconel button hook nozzle and attached thermocouple and pitot tube. The probe was maintained at a temperature of $250^{\circ}\text{F} \pm 25^{\circ}\text{F}$. After the probe, the gas passed through a heated glass fiber filter (Reeve Angel 934 AH filter paper). Downstream of the heated filter, the sample gas passed through a water-cooled module, then through a sorbent module containing approximately 25g of XAD-2 resin. The XAD module, which was kept at a temperature below 20°C , is followed by a series of four impingers. The first impinger, acted as a condensate reservoir connect to the outlet of the XAD module, and was modified with a short stem so that the sample gas did not bubble through the collected condensate. The first and third impingers were empty, the second contained 100 mL of DI water, and the fourth contained a known weight of silica gel. All connections within the train were glass or Teflon and no sealant greases were used. The impingers were followed by a pump, dry gas meter, and a calibrated orifice meter.

Readings of flue gas parameters were recorded at every sampling point during the sampling traverse. In the event that steady operation was not maintained, or there were atypical fluctuations in monitored gas parameters (CO , O_2), the testing was stopped until these conditions were stabilized. Steady operation of the pyrolysis unit was the responsibility of Pyrolysis Systems, Inc., personnel, but the flue gas parameters and composition was monitored by GCA. Any changes were noted and relayed to PSI personnel so that appropriate action could be taken.

Sampling was conducted while traversing the MM5 train across the two diameters shown in Figure 5-5. The stack satisfied the 8 and 2 criteria for a minimum number of sampling points and a twelve point test was selected for these runs.

Prior to sampling, all gas-contacting components of the train were washed withalconox and water, thoroughly rinsed with DI water, and oven dried at 110°C for at least 1 hour. Immediately prior to use, the components were rinsed with hexane. At each test point within the stack, all necessary train parameters were measured. All field data sheets are included in the appendix.

Leak checks on the MM5 sampling train were performed before and after each sampling run. The sample train leak checks and leakage rate (if applicable) were documented on the field test data sheet for each respective run.

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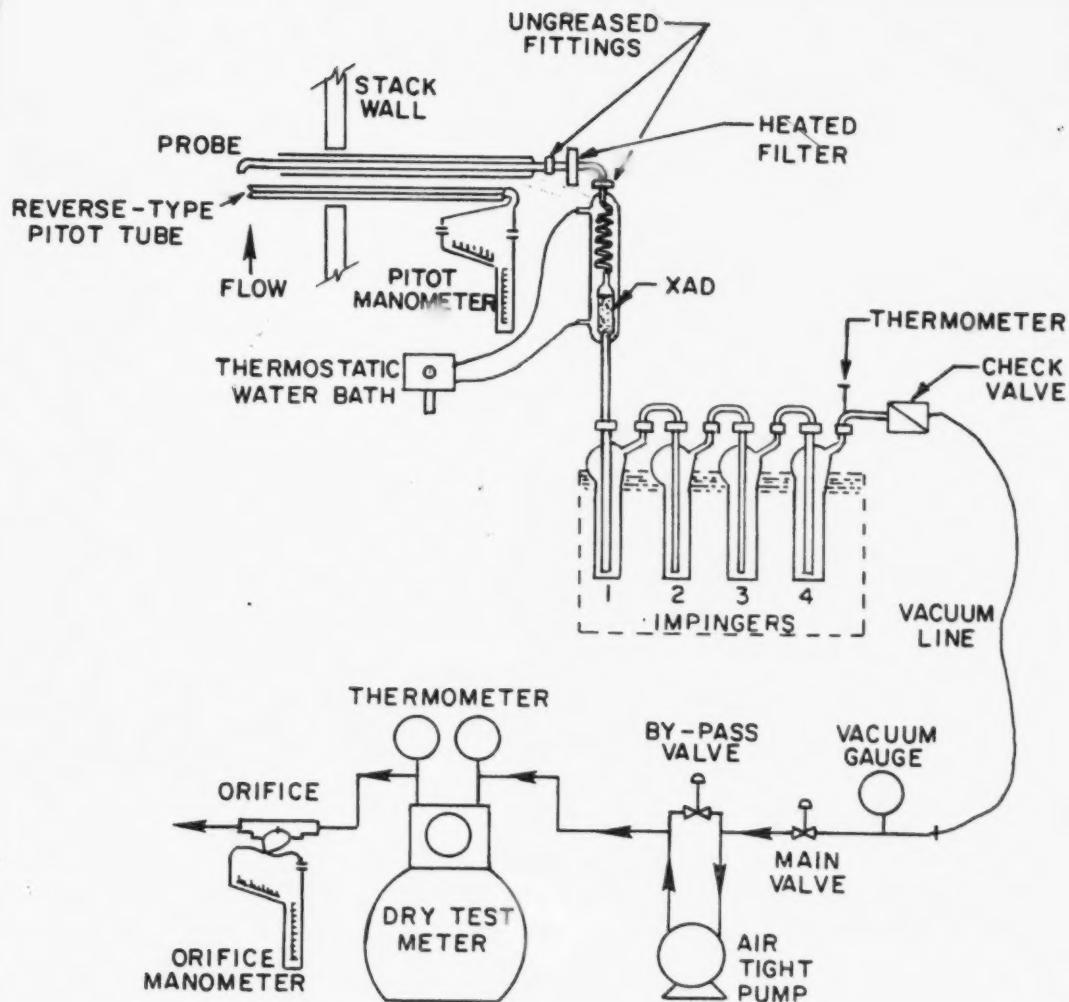
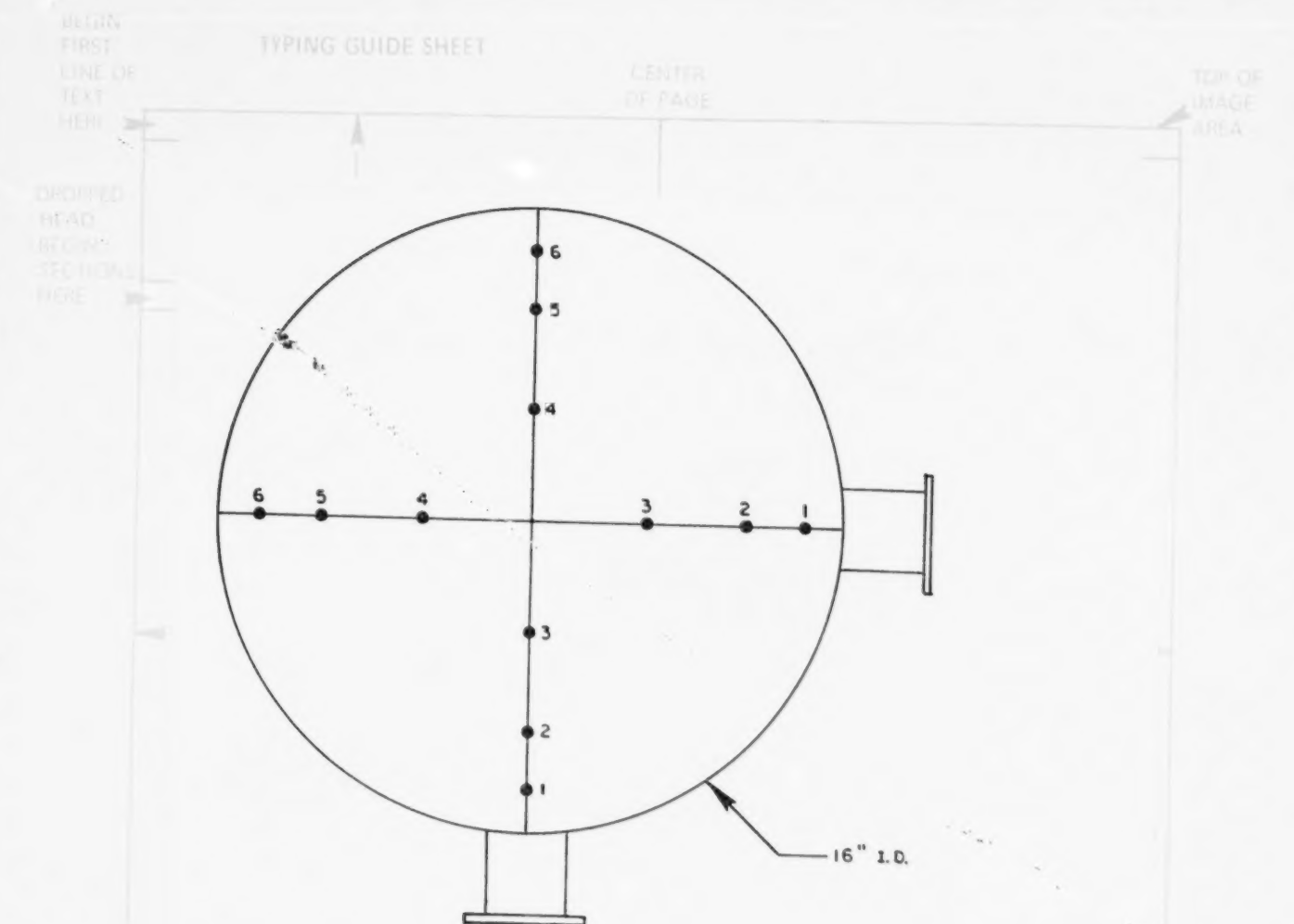


Figure 5-4. Modified Method 5 train.



<u>Point</u>	<u>Distance from Wall (in.)</u>
1	0.70
2	2.34
3	4.74
4	11.26
5	13.66
6	15.30

Figure 5-5. Modified Method 5 sample point locations.

Following completion of each test run, the MM5 trains were transported to the onsite trailer for recovery. Recovery procedures differed depending on whether the 4-hour MM5 samples were to be analyzed for PCDD/PCDF and PCBs or semivolatiles. The PCDD/PCDF and PCB train was analyzed solely for those parameters and not for particulate emissions. The recovery procedures outlined in the Quality Assurance Project Plan were followed.

Because the particulate catch from the MM5 trains intended for semivolatile GC/MS analyses were to be first used to determine particulate emission rates, a slightly more involved recovery procedure was required. The recovery technique was conducted on those 4-hour MM5 runs not intended for PCDD/PCDF analyses. The procedure followed during this recovery was as outlined in the Quality Assurance Project Plan.

After the total particulate catch was determined, the acetone rinse residue was redissolved in hexane and the organic analyses proceeded as described in the analytical section of this report.

Filters for all modified Method 5 trains were tare-weighed prior to use for the determination of particulate loading. These filters were then placed in sealed glass containers for shipment to the test site.

Sorbent resins used in MM5 sampling trains require extensive preparation and quality assurance measures prior to use in the field to eliminate the possibility of sample bias due to sorbent contamination. The XAD-2 resin used in this sample train was obtained from Supelco, Inc. The resin was precleaned by soxhlet extraction using the sequence outlined in the IERL-RTP Procedures Manual: Level 1 Environmental Assessment as described in the Quality Assurance Project Plan. The XAD-2 resin used in the MM5 train for PCDD/PCDF collection was soxhlet extracted overnight in toluene in addition to the sequence outlined in the IERL-RTP Level 1 assessment procedure.

Gaseous HCl--

Sampling was conducted at the postflare sampling location to quantify HCl emissions during each stage of this test program. The method used in collecting the gaseous HCl was the Texas Air control Board (TACB) method with deionized water in the first two impingers as the absorbing solutions.

The sampling train is shown in Figure 5-6. It consists of a probe liner, an impinger train with DI H₂O and silica gel, a pump, a dry gas meter, and a manometer. Chloride was determined onsite colorimetrically during the CCl₄ burns. After the 4 hour PCB endurance burns, the samples were transported back to GCA for analysis.

Leak checks on the HCl sampling train were conducted before and after each sampling run. The sample train leak checks and leakage rate (if applicable) are documented on the field test data sheet for each respective run.

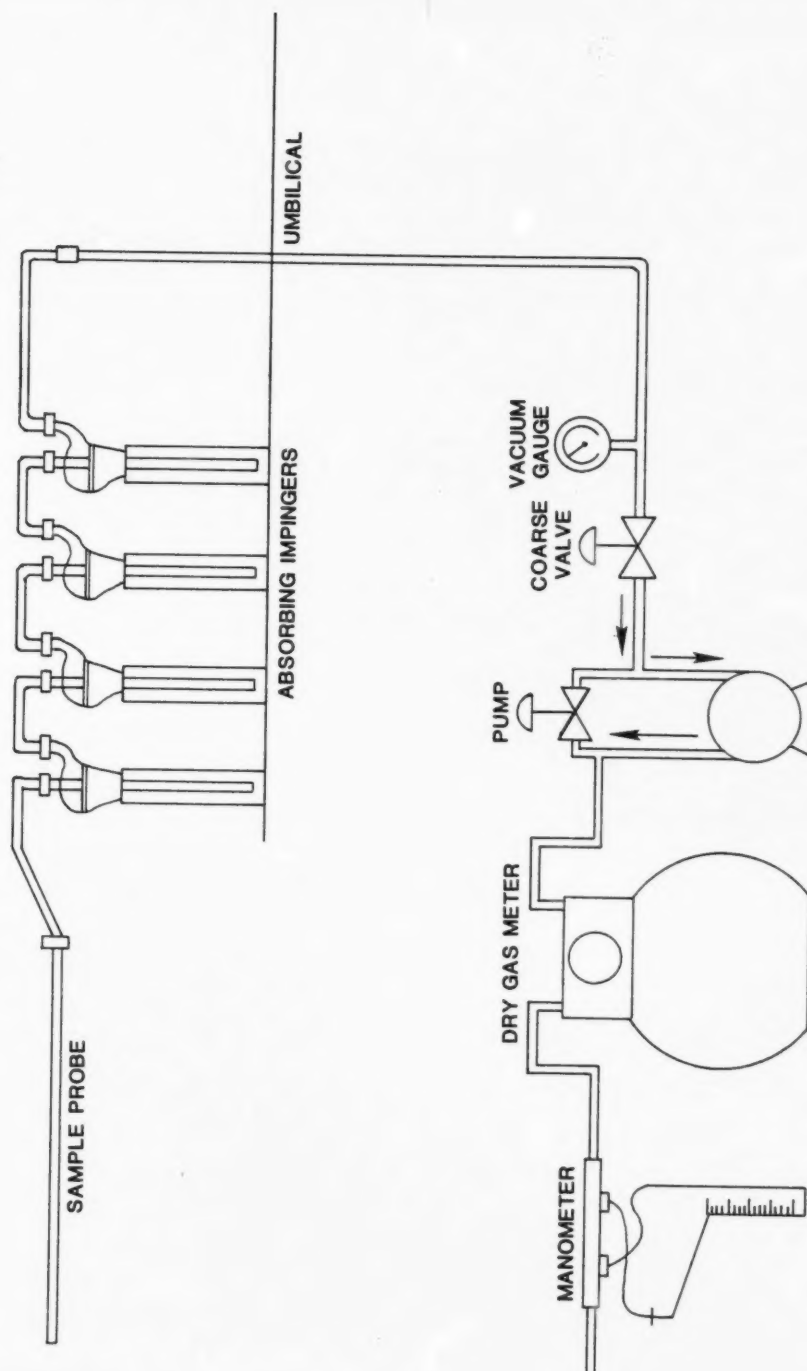


Figure 5-6. Gaseous HCl sampling train.

Moisture (H₂O)--

Moisture in the postflare stack gas was determined by impinger weight gain from the beginning of the test run to the end. In this method, initial and final weights of the impingers are obtained by weighing on a balance accurate to 0.1 gram.

Temperatures and Flow Rates--

During the 1 hour CCl₄ test runs, a pressure transducer and thermocouple were used to continuously monitor stack gas velocity and temperatures at the postflare location. Monitoring the preflare location was attempted during the first CCl₄ burn but was aborted following several hydrogen flarebacks in the preflare pipe as well as experiencing heavy carbon plugging of the pitot tube.

Flow rates and temperatures during the 4 hour PCB endurance test runs were measured during the MM5 sampling when velocity and temperature readings were recorded at each sampling point. The semivolatile sampling train measurements were used in calculating the pollutant emission rates during the run. The flow rates calculated from these measurements were in close agreement (<5 percent difference) with those flow rates measured with the PCDD/PCDF sampling probe borrowed from the Ontario Ministry of the Environment.

ANALYTICAL METHODS

- Waste Feed
- Reactor Hearth Ash
- Spent Scrubber Water
- Postflare Product Gas

Volatile Organic Compounds

The identification of additional compounds detected by the GC-MS system were determined using a computer search of the NBS/EPA/NIH library to provide tentative spectral matches. These, as well as unknown spectra, were reviewed for major peaks and fragmentation patterns. Further identifications were made by the operator and verified by comparison of available reference spectra (NBS/EPA/NIH library) to the background corrected component spectra. Component concentrations were calculated relative to the closest eluting internal standards. All values represent approximations due to inherent variabilities in component response factors in the absence of reference materials.

The following steps were taken to detect contamination introduced in sample handling or analysis:

1. Analysis of field biased blanks--Deionized water taken to the field and carried through the storage and analysis procedures were analyzed.
2. Daily analysis of method blanks--A sample of deionized water was analyzed. This detects contamination introduced by the purge gas or the tubing in front of the trap.
3. After analysis of a high (>200 ppb) level sample, a blank of deionized water was analyzed to ensure that contamination of subsequent samples by carryover had not occurred.

Semivolatile Organic Compounds

Aqueous samples collected for semivolatile organic compound determination were analyzed in accordance with EPA Method 625. Surrogate compounds were added to the samples and then serially extracted with methylene chloride at a pH greater than 11 and again at pH less than 2, using a separatory funnel. The methylene chloride extract is dried and subsequently concentrated to a volume of 1 to 2 mL. The concentrated extract is then analyzed by gas chromatography/mass spectrometry. Particulate matter was separated from aqueous samples via filtration and subsequently extracted with a soxhlet apparatus using methylene chloride. The extract was then subjected to concentration and GC/MS analysis as described for aqueous aliquots.

POSTFLARE STACK GAS

Modified Method 5 (for Semivolatile Organics)--

Method 5 train samples were analyzed by GCA for semivolatile organic compounds. Each train, as noted earlier, produced four types of samples: 1) particulate collected on a filter; 2) probe rinses; 3) XAD sorbent samples; and 4) impinger/condensates. Figure 6-1 shows the analytical flow scheme.

The recovered filters and probe rinses were prepared for gravimetric analysis. Once particulate weights were recorded, catches and probe rinses were combined with the appropriate XAD sample and extracted. Three samples were extracted composited and analyzed from each MM5 Train:

- impinger waters and condensate,
- probe rinse (front half) and filter,
- back half rinses and XAD adsorbent.

The latter two samples were surrogate-spiked with d_5 -nitrobenzene, 2-fluorobiphenyl, d_{14} -terphenyl, d_5 phenol, 2-fluorophenol, and 2,3,6-tribromophenol, and then soxhlet-extracted for a period of 24-hours in methylene chloride.

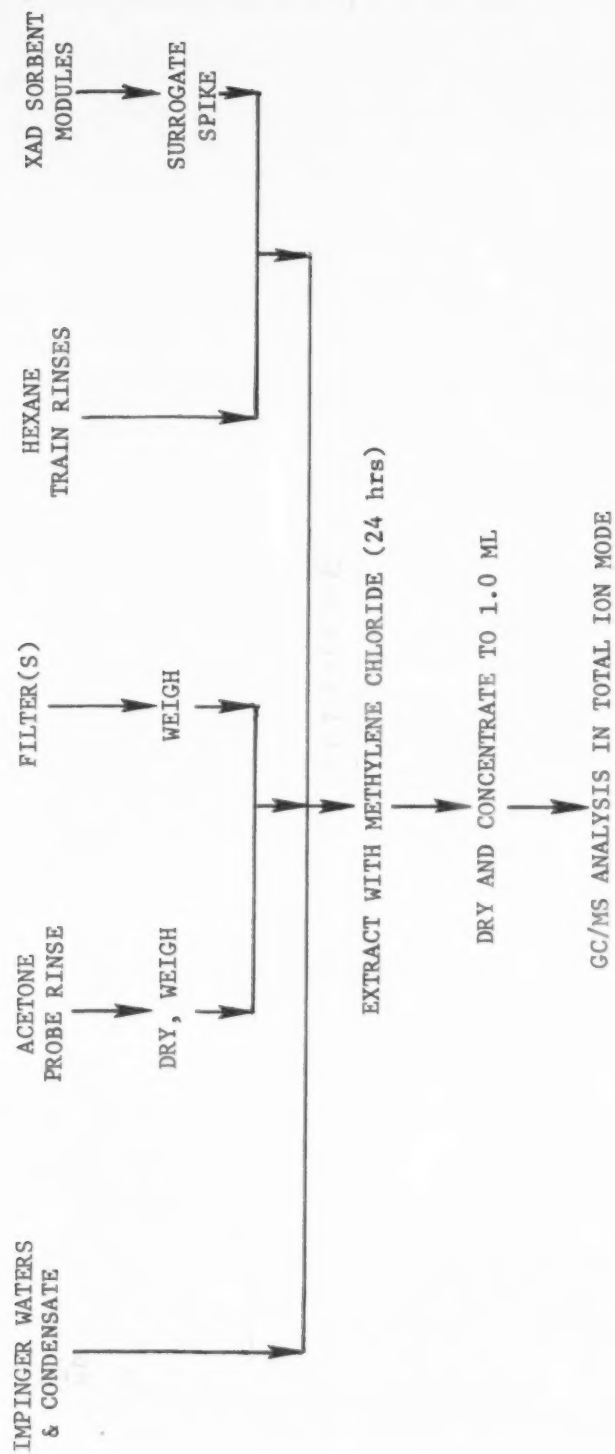


Figure 6-1. Modified Method 5 train organic analysis flow scheme.

Impinger water and condensate samples were extracted three times with methylene chloride. The extracts were then dried over sodium sulfate combined with the XAD/filter extract and concentrated via Kuderna Danish apparatus to 1.0 mL.

The combined extract was scanned for semivolatile organics, using capillary column gas chromatography/mass spectrometry (GC/MS) and the internal standards. All component spectra were collected in the total ion mode. GC/MS instrument operating conditions are listed in Table 7-8 of the Quality Assurance Project Plan. Identification of peaks in the total ion current profile (TICP) was made using retention times and spectral matches to standards. Additional compounds were identified using a forward search of the NBS Library of Mass Spectral Data supplemented by manual comparison of component spectra with the library-derived spectra.

Chlorides--

Samples for chloride analyses were prepared by ignition in an oxygen atmosphere in a Parr bomb. Residues were collected and analyzed using a Technicon AutoAnalyzer II according to the protocol set forth in Method 325.2 (Methods for Chemical Analysis of Water and Wastes).

SECTION 7

QUALITY ASSURANCE/QUALITY CONTROL

INTRODUCTION

Quality Assurance/Quality Control (QA/QC) protocols followed in this program were based upon routine sampling and analytical practices and the revised Quality Assurance Project Plan (QAPP) entitled Performance Testing of the Pyrolysis Systems, Inc. Plasma Pyrolysis Unit, submitted for this program on February 4, 1985. This Quality Assurance section will detail areas where changes in laboratory and/or field procedures were made. In order to facilitate review of pertinent QC data, this section will roughly follow the outline of the QAPP.

PROJECT DESCRIPTION

Stage II Tests

Preflare product gas was not sampled for CCl_4 , HCl , or monitored for velocity and temperature. The high carbon and moisture content of the gas stream were not conducive to such measurements. A pitot tube/pressure transducer and thermocouple were mounted in the sample port but were removed because hydrogen flarebacks created a hazard at the preflare sampling location. The hydrogen flarebacks were essentially ignition of the preflare product gas from the flarehead back to the I.D fan within the trailer, resulting in a minor explosion inside the fan. No further testing was attempted at this location. However, the ports were periodically used for obtaining carbon samples, between runs.

The availability of reactor ash after test runs was limited due to the lengthiness of the cool down period and the difficulty associated in obtaining the sample. This necessitated the removal of plasma torch, the waste feed ring, coolant flange, and graphite core.

Stage III Tests

Two test series (2 and 3) were scheduled for the Stage III level of testing involving the destruction of PCB containing liquid waste feed. In the effort to complete Stage II Test Series 1 and Stage III Test Series 2 in February 1985, funding was depleted due to the length of time the crew was required to be onsite. These delays were caused by equipment problems within the pyrolysis system, ones which, largely, could not have been foreseen prior

to actual test attempts on the different waste feeds. Stage II testing was completed after several attempts. Stage III Test Series 2 underwent several attempts in February and March, 1985 at completing a single test run but the efforts were unsuccessful after repeated pyrolysis system equipment problems. Testing was suspended until the equipment problems could be corrected. It was decided that a local test company would conduct the Stage III Test Series 2 testing on an "on call" basis. This testing was completed in January 1986.

GCA was contracted to conduct the Stage III Test Series 3 PCB endurance tests in 1986, which were to be a minimum of 6 hours in duration. The first burn attempt lasted only 115 minutes. It was decided at that point by NYSDEC and PSI that shorter test burns would be necessary because it was questionable as to whether the system would stay online for the duration of a full 6-hour test. Rather than risk another aborted run, the sampling time was shortened to 240 minutes (4 hours). Two successful test burns were then conducted, finishing Stage III Test Series 3 and GCA's involvement in Phase II activities. Stage IV testing, as described in the QAPP, was cancelled.

PROJECT ORGANIZATION AND RESPONSIBILITIES

During the course of this program, three major changes were made in GCA's project and quality assurance organization. Mr. Paul Exner replaced Dr. Paul Fennelly as Program Manager. Ms. Joan Schlosstein replaced Ms. Andrea Cutter as Analytical QC Coordinator, and Mr. Howard Schiff replaced Mr. Richard Graziano as Measurements QC Coordinator.

PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

During the 4-hour PCB endurance tests, the continuous emission monitors and orsat gas analyses were the only measurements made onsite. Precision estimates could not be made on these measurements with any consistency because there were so few data points. Only two complete test runs were conducted and these for only four hours. Accuracy estimates of the CEMs were not made due to no provision being made for audit gas cylinders under this program. A summary of measurement precision, accuracy, and completeness goals and accomplishments is shown in Table 7-1. The hourly orsat data for Runs 3-2 and 3-3 did yield O₂ mean concentrations of 14.0 and 15.3 percent, respectively, and CO₂ mean concentrations of 5.1 and 4.3 percent, respectively. Standard deviations for hourly O₂ readings were 1.04 and 0.15 percent for the two runs. CO₂ concentrations yielded standard deviations of 0.64 and 0.38 for the two runs. The true precision of the measurements cannot be estimated due to there being only four hourly measurements made per run and no simultaneous measurements made.

Since insufficient sample volume was available for replicate aliquots in most cases, analytical precision could not be determined. Analytical accuracy was determined through the analysis of EPA Environmental Monitoring and Support Laboratory (EMSL) Quality Control Samples and the analysis of matrix and surrogate spiked sample aliquots. Results of these analyses broken down by parameter are presented in Tables 7-2 through 7-6 and are discussed below.

TABLE 7-1. SUMMARY OF CEM PRECISION, ACCURACY, AND COMPLETENESS

Measurement (parameter)	Precision		Accuracy		Completeness	
	Goal (%)	Actual ^a	Goal(%)	Actual ^b	Goal (%)	Actual (%) ^c
Oxygen (MSA 802)	<0.5 (v/v)	NA	15	ND	95	99
Carbon Dioxide (Horiba PIR 2000)	<0.5 (v/v)	NA	15	ND	95	99
Carbon Monoxide (Horiba PIR 2000)	<2.5 (v/v)	NA	15	ND	95	99
Oxides of Nitrogen (TECO 10A)	10 RSD	NA	15	ND	95	99
Oxygen (EPA Method 3)	0.6 (v/v)	NA	3.0	ND	95	100
Carbon Dioxide (EPA Method 3)	0.6 (v/v)	NA	3.0	ND	95	100

^aPrecision estimates could not be determined from only two complete test runs (four data points).

^bNo audit gas cylinders were provided for this program. Original scope of program changed greatly - only two complete test runs.

^cSix minutes of CEM data were lost during Run 3-3 due to purging of condensate from the sample line.

TABLE 7-2. ANALYSIS OF A LABORATORY CONTROL
SAMPLE FOR CHLORIDES

QC sample	Expected (mg/L)	Recovered (mg/L)	Percent recovery
WP-882-1	8.52	9.18	108

TABLE 7-3. ANALYSIS OF A MATRIX SPIKE INTO SCRUBBER WATER
FOR VOLATILE ORGANICS

Compound	Concentration ($\mu\text{g/L}$)		Percent recovery	QA Objective (Percent Recovery)
	Expected	Recovered		
1,1-Dichloroethene	50	52	104	60-180
Trichloroethene	50	43	86	60-140
Chlorobenzene	50	45	90	60-140
Toluene	50	44	88	60-140
Benzene	50	49	98	60-150

TABLE 7-4. ANALYSIS OF A SURROGATE SPIKE INTO
SCRUBBER WATER FOR VOLATILE ORGANICS

Compound	Percent Recovery		Average	QA Objective (Percent Recovery)
	Run 2	Run 3		
Toluene-D8	96	99	98	none
Bromofluorobenzene	121	109	115	
1,2-Dichloroethane-D4	96	116	106	

TABLE 7-5. ANALYSIS OF SEMIVOLATILE ORGANIC MATRIX
SPIKED COMPOUNDS (PERCENT RECOVERIES)

Compound	Filtrate Water	Filter	XAD	QA Objectives
1,2,4-Trichlorobenzene	91	91	84	20-110
Acenaphthene	100	96	84	30-140
2,4-Dinitrotoluene	114	110	86	20-90
Pyrene	128	109	71	30-150
N-nitrosodi-n-propylamine	103	93	76	40-130
1,4-Dichlorobenzene	92	99	73	20-110
Pentachlorophenol	74	80	51	10-110
Phenol	34	75	38	20-90
2-Chlorophenol	66	80	48	20-110
4-Chloro-3-methylphenol	68	75	40	20-110
4-Nitrophenol	29	90	58	10-120

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TABLE 7-6. ANALYSIS OF SEMIVOLATILE ORGANIC SURROGATE SPIKED COMPOUNDS IN SAMPLE ALIQUOTS

Sample ID	Percent Recovery					
	Nitrobenzene -D ₅	2-Fluoro- biphenyl	Terphenyl D ₅	Phenol D ₅	2-fluoro- phenol	2,4,6 Tri- Bromo- phenol
Scrubber Water Method Blank	81	99	86	57	25	83
Scrubber Water Matrix Spike	78	98	79	49	21	96
Run 1 Scrubber Water	71	104	63	81	31	78
Run 2 Scrubber Water	59	104	58	80	50	86
Run 3 Scrubber	64	102	50	49	50	81
XAD/Filter Blank	133	157	104	158	41	85
XAD Matrix Spike	130	154	93	142	69	116
Run 1 M-5 Blank	128	147	95	148	68	85
Run 1 M-5	129	168	82	99	30	164
Run 2 M-5 Blank	138	154	97	162	40	87
Run 2 M-5	137	169	68	0*	10*	147
Run 3 M-5 Blank	102	150	99	125	13	103
Run 3 M-5	131	147	81	7*	4*	96
QA Objectives	41-120	44-119	33-128	10-110	10-130	none

*Matrix interference

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Completeness, defined as the percentage of all measurements whose results are judged valid, was estimated to have achieved the goal of 95 percent. Wherever possible, reference methods and standard sampling procedures were used as stated in the QA Plan to ensure comparability with other representative measurements made by GCA or another organization.

SAMPLING PROCEDURES

Semivolatile, PCDD/PCDF Trains

Several quality control problems occurred during the sampling program conducted in February 1986. These problems consisted of nonisokinetic sampling, pitot tube and sampling train leak checks, configuration of the PCDD/PCDF train probe tip, and the existence of blockage within the stack due to the simultaneous sampling requirements of the program.

Simultaneous sampling of a small area (i.e., a 16-inch diameter stack) with two 3-inch diameter water-cooled sampling probes, would lead to flow blockage at the sampling plane. This blockage causes a greater velocity of the flue gas passing the pitot tubes and sample nozzle than would be measured using smaller diameter probes or a single probe. The effect of the blockage on the velocity readings by each individual train could not be ascertained. However, the effect on each train would be equal as the velocities were in close agreement. For example, during Run 3-3, the velocity and flow rate measured by the semivolatile train was 3,843 ft/min and 1,264 ft³/min, respectively. The same measurements taken by the PCDD/PCDF train were 3,797 ft/min and 1,234 ft³/min, respectively. The concerns regarding the possibility of flow blockage were presented to EPA and New York State technical personnel prior to the commencement of Stage III testing. They concurred that although flow blockage may exist within the stack, the operational and time constraints of the program were such that simultaneous sampling for semivolatile and chlorinated organics (PCDD/PCDF) was necessary.

The pitot tube head of the PCDD/PCDF probe was positioned approximately 2 inches behind the quartz sample nozzle due to the length of the integral quartz probe liner supplied with the probe. The method calls for close alignment of the pitot tips and sampling nozzle. No other configuration of the probe was possible without extensive modifications of the probe and sampling hot box. This misalignment usually would have an effect on the isokinetic sampling as the velocity at the pitot head would not necessarily be the same as the velocity at the sample nozzle. However, the velocity profile of the stack was fairly flat across each line of traverse with very little variation between the points. Therefore, the effect of the misalignment on isokinetic sampling was not as great as if the velocity profile was skewed or erratic.

All sampling train and pitot tube leak checks were conducted prior to, and on the completion of each run. The leak rate limit for the sampling train of <0.02 cfm was met for all runs conducted. However, the leak check on the PCDD/PCDF sample train following Run 3-2 was conducted from the front-half of the filter, because the quartz nozzle was thermally the most weakened at two

or three points approximately 3 inches back from the 90° bend. After cooling and an attempted leak check, this portion broke off completely and fell to the ground. The nozzle was not rinsed into the sample container because of the possible contamination of the sample from carbon deposits on the ground. The probe section was recovered. The train leak check was then conducted from the front of the filter holder. It is assumed that the breakage occurred because of: 1) burnthrough of the liner occurred within the stack due to the extremely high temperatures, and 2) upon removing the probe from the stack, the nozzle cracked through from thermal shock resulting from the very cold ambient temperatures. The amount of particulate matter lost in the nozzle was determined to be negligible due to the very low grain loading within the flue gas.

The post-run PCDD/PCDF train pitot tube leak check for Run 3-2 failed to meet the leak rate requirements on the impact side of the pitot. The high stack temperature caused a burnthrough in the probe, including the quartz liner and pitot tubes. It is assumed that this burnthrough occurred during the final half-hour of the run when temperatures were highest. Theoretically, the test run should be voided. However, the velocity head measured by both trains were in fairly close agreement (0.36 in. H₂O for the semivolatile train and 0.37 in. H₂O for the PCDD/PCDF train during Run 3-2). If it is assumed that the burnthrough occurred in the final minutes of the test run, the effect on overall velocity measurements would be minimal.

There was a problem with nonisokinetic sampling of the flue gas during Test Runs 3-1 and 3-2 (semivolatile train) and Runs 3-2 and 3-3 (PCDD/PCDF train). A test run is valid and no correction or invalidation is required when the isokinetic ratio is between 0.90 and 1.10. Due to the variability of the waste feed and resultant product gas constituents, the stack temperatures after the flare varied widely. The operators apparently were unable to keep up with the temperature changes when setting their nomographs. The nonisokinetics of the involved sampling runs affects only the collection of particulate matter and does not affect the collection of compounds in the vapor state. Vapor state material is only affected by concentration stratification across the sampling plane which is alleviated by multipoint sampling across that plane. Particulate concentrations and emission rates can be corrected for a nonisokinetic condition by multiplying these values by the isokinetic ratio. This results in a value that would have been obtained, had the sample been obtained isokinetically. This correction is given in Table 7-7.

TABLE 7-7. PARTICULATE MATTER EMISSIONS CORRECTION

	Run 3-1	Run 3-2	Run 3-3
lb/hr concentration	0.0952	0.0366	0.0520
Isokinetic ratio	0.8190	1.112	1.093
lb/hr, corrected	0.0780	0.0407	0.0568

As can be seen by the above corrections, the change in emission rates is negligible and does not affect the data appreciably.

VOST, HCl, Fixed Gases

No problems were experienced when sampling for volatile organics (VOST), HCl, fixed gases (EPA M3), or fixed gases (CEMs). During Run 3-3, however, approximately 6 minutes of CEM data was lost when condensate built up in the sample line and required purging.

Chlorides

Quality control procedures for chlorides included the analysis of laboratory control samples and field blanks.

Precision was not measured. Accuracy, measured as the percent recovery of laboratory control samples was estimated at 108 percent. These results are presented in Table 7-2. No precision or accuracy goals were established for chloride analysis.

Volatile and Semivolatile Organics

Quality control procedures for volatile and semivolatile organics determinations included the analysis of matrix and surrogate spiked sample aliquots. Results of these analyses, used as an indication of accuracy, are presented in Tables 7-3 through 7-6. QA objectives are presented alongside experimental values for comparison. Completeness objectives of 95% were achieved.

Deviations From QA Plan

In an effort to cut program costs, precision of analytical measurements through the analysis of replicate sample aliquots was not performed. Recoveries of surrogate spiked compounds did not meet QA objectives in all cases.

SAMPLE CUSTODY

Sample Chain-of-Custody was maintained throughout the program. These procedures are described in Section 5 of the Quality Assurance Project Plan prepared for this program. It should be noted that the post-flare stack gas volatile organic samples were allowed to become warm during shipment. In addition, the holding times for these samples were exceeded. These samples were not analyzed as the results could have been deemed erroneous and unsupportable.

CALIBRATION PROCEDURES AND FREQUENCY

Calibration procedures described in Section 6 of the QA Plan were followed during this sampling program.

ANALYTICAL PROCEDURES

Analytical procedures summarized in Table 7-2 of the QA Plan were followed during this program. Several comments on the QA Plan were made in the February 21, 1986, EPA memo from Charles Porfert, Deputy Quality Assurance Officer, regarding analytical procedures (comments 1, 2, and 3). Comment 1 requested information on QA objectives for precision, accuracy, and completeness. The analytical QC methods used are described in Section 9 of the QA Plan; percent recovery objectives are given in Table 3-1 of Section 3; and detection limits are not required. Comment 2 regarded certain EPA analytical methods which should be used for analysis of sediment samples. Comment 3 requested the use of EPA Method 314B for hardness. However, GCA did not have the reagents necessary to perform this procedure and, in order not to delay the program, Method 314A was used.

DATA REDUCTION, VALIDATION, AND REPORTING

Data reduction, validation, and reporting procedures described in Section 8 of the QA Plan were followed during this program.

INTERNAL QUALITY CONTROL CHECKS

Internal QC procedures described in Section 9 of the QA Plan were followed during this program, with the exception of duplicate sample analyses which were not performed.

PERFORMANCE AND SYSTEM AUDITS

Analytical performance was audited through the use of internal quality control checks described in Section 9 of the QA Plan. In addition, the laboratory participated in EPA Water Pollution (WP) Study 016 and water supply (WS) Study 018 during the period of performance of this work. The results of these analyses, for compounds pertinent to this test program, can be found in Appendix B. No system audit was conducted during the period of performance of this work.

PREVENTIVE MAINTENANCE

Preventive maintenance procedures described in Section 11 of the QA Plan were followed during this program.

ASSESSMENT OF PRECISION, ACCURACY AND COMPLETENESS

Analytical precision was not reported. Accuracy assessments were based on the results of analyses of EPA Standard Reference Materials and of matrix spiked samples and reported in terms of percent recovery which was calculated as shown below:

$$\text{Percent Recovery} = 100 \left(\frac{\text{Measured Value}}{\text{True Value}} \right)$$

The following formula was used to estimate completeness:

$$C = 100 \left(\frac{V}{T} \right)$$

where: C = Percent completeness,

V = Number of measurements judged valid, and

T = Total number of measurements.

CORRECTIVE ACTION

There were no Corrective Action Request forms initiated in regard to this program.

REFERENCES

1. Quality Assurance Project Plan, "Performance Testing of the Pyrolysis Systems, Inc. Plasma Pyrolysis Unit," Final Version, February 1985, GCA/Technology Division.
2. "Presentation of a Method for the Selection of POHCs in Accordance with the RCRA Interim Final Rule, Incineration Standards," January 23, 1981, Office of Solid Waste.